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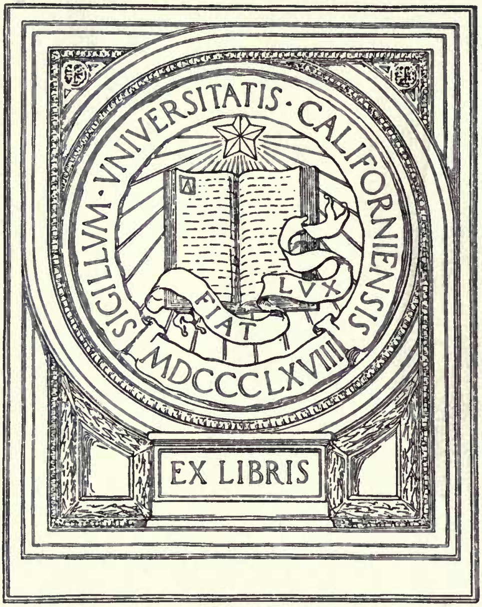

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ORGANIC CHEMISTRY

FOR THE

LABORATORY

BY

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Second Edition, Revised and Enlarged

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PREFACE TO SECOND EDITION

In preparing a second edition of this book, Chapters on the Analysis of Organic Compounds, on General Operations, on Ethers, on Hydroxy and Ketonic Acids and on Carbohydrates have been added, and thirty new preparations have been included. The Chapters in the book have also been rearranged to correspond more nearly with the order used in the author's text-book. It is hoped that this rearrangement will not interfere with the use of the book by those who prefer some other text-book as the basis for their instruction.

The tables for nitrogen have been recalculated on the basis of modern values for the weight of one liter and for the coefficient of expansion of nitrogen. Some similar tables in common use are about 0.4 per cent. in error because old, erroneous values for these constants were used in their preparation.

It is more true than before that the number of preparations given is too great for the average student to complete. To meet this difficulty classes may be divided into groups of four to six students and each group be required to complete nearly all of the preparations in the book, the preparations assigned to individuals being different. Each individual of the group should be expected to become familiar with all of the fundamental principles of the preparations made by the members of his group. By this method the knowledge acquired in a given time may be considerably increased.

I wish to express my obligation to Professor R. S. Curtiss, Dr. C. G. Derick and Dr. L. H. Cone who have made many valuable suggestions with regard to the revision; also to Professor Edward Hart, who furnished the directions for the distillation of wood and separation of the products formed, as these processes are carried out in his laboratory at Lafayette College.

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PREFACE TO FIRST EDITION

The science of organic chemistry rests, for its experimental foundation, on the preparation, usually by synthetical means, of pure compounds. Without a knowledge, based on personal experience in the laboratory, of the relations involved and the methods which may be used in such preparations, no satisfactory knowledge of the science can be acquired. It has been the purpose of the author in writing this book to classify the most important of the laboratory processes which have been used in the development of the science and to illustrate them by concrete examples.

Two distinct purposes have been kept in view. The first has been to furnish the beginner with sufficiently full and accurate directions and clear, concise, theoretical explanations of processes which have been found successful in practical laboratory experience. The second object has been to furnish the more advanced student and practical worker with a guide which will aid him in the selection of processes which are likely to be successful for the preparation of compounds which he may desire to use.

It is for this second reason, partly, that the number of preparations given is considerably greater than it would be profitable for the average student to prepare, and that the references to the literature have been made quite full.

The student who uses the book is very earnestly advised to begin each preparation with a careful study of the directions given, and also of the literature of the subject. For the time being, he should make himself thoroughly familiar with all of the important relations of the substance with which he is working, and with other methods of preparation which might be used. Comparatively few preparations carefully studied in this way will be of greater value than a much larger number mechanically executed by simply following the directions of the book. The successful student must be able to use intelligently the larger handbooks, especially that of Beilstein, and the original sources in chemical journals. It need scarcely be remarked that a satisfactory working knowledge of organic chemistry cannot be acquired without the ability to use German books.

In some cases it may be well to undertake the preparation of analogous substances in place of the ones which are given. The majority of the processes described should be viewed from the standpoint that they are applicable to many other similar cases, though slight modifications are often necessary and as to that the student should satisfy himself by examination of the literature before he goes on with his work. In research work chemists very often help themselves by a careful study of the properties of bodies related, or analogous, to those which they wish to prepare, and the habit of making comparisons of this kind is very valuable.

It is not the intention of the author that the order of the book should be necessarily, or, indeed, usually followed by the student. He has a very firm conviction that laboratory work of the sort provided for in this book should always accompany the lecture-room or text-book work in organic chemistry, and that the frequent lack of interest in the subject is often due to the fact that the laboratory work is given a year or two after the lectures, or that it is omitted altogether. If the book is used in conjunction with the usual course of lectures to beginners, as it is hoped that it may be, topics will naturally be selected in the same general order as that followed in the lectures or text-book.

The discussion of special topics, such as crystallization, filtration, distillation, distillation under diminished pressure, extraction, etc. has been given in connection with preparations when their use is required. Frequent references to these discussions are given elsewhere, and they may also be readily found by means of the index.

The author wishes to acknowledge his indebtedness to the somewhat similar works of Levy, Gattermann, Erdmann, and E. Fischer for many suggestions; also to a little book by Drs. A.

A. Noyes and S. P. Mulliken on the "Class Reactions of Organic Substances," for some suggestions in writing the chapter on the qualitative examination of organic substances. He also desires to express his thanks to Mr. W. E. Burk, who prepared the drawings for the book, and to Mr. J. J. Kessler, Jr., who has tested many of the directions for preparations in the laboratory. I wish also to express my sincere thanks to Dr. J. Bishop Tingle, who has read carefully all of the proofs, and has made many valuable suggestions.

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Chapter I

ANALYSIS OF COMPOUNDS OF CARBONS

Literature.—H. Meyer: Analyse und Konstitutionsermittelung organischer Verbindungen, 2 Auflage, pp. 146-320; Benedict: Amer. Chem. J., 23, 323 and 324; J. Am. Chem. Soc., 21, 389; Mabery and Clymer: *Ibid*, 22, 213; Dennstedt: Anleitung zur vereinfachten Elementaranalyse, 2 Auflage, 1906, also Ber., 41, 600; Z. anal chem., 42, 417.

Determination of Carbon and Hydrogen.—The apparatus required for the determination of carbon and hydrogen in a compound containing only these elements or these elements with oxygen or nitrogen, or both, is as follows:

1. A combustion tube 10 to 12 cm. longer than the combustion furnace. The ends should be cut square across and rounded, without narrowing, in the blast flame, heating at first a little distance from the end. The tube should be 12 to 15 mm. in internal diameter, of infusible glass and with walls about 2 mm. thick.

2. Copper oxide, granulated or wire form.

3. A copper spiral 10 to 12 cm. long, two spirals 2 to 3 cm. long, and one 5 to 6 cm. The two short spirals should fit the tubes closely, the other two loosely. Each spiral is made by wrapping pure copper wire gauze around a stiff copper wire, which should be bent to a loop or hook at one end. The long copper spiral is required only for compounds containing nitrogen and should be oxidized superficially by holding it in the flame of a Bunsen burner and then reduced by plunging it while hot into a test-tube containing about one-half cc. of pure methyl alcohol. The tube should be stoppered till the spiral has cooled and the latter dried at 150° and placed, while hot, in a desiccator.

4. A 105 mm. U-tube filled with calcium chloride. The calcium chloride should be in granular form and its solution in water must not react alkaline. The form of tube shown in Fig. 1 is most suitable. The bulb A is so constructed that the water col-

lecting in the bulb cannot run into the portion of the tube containing the calcium chloride. The rubber stopper at B must fit tightly and should be cut even with the top of the tube and covered with sealing wax. It should completely fill that portion of the tube above the side arm C so that the current of gas through the tube will be direct. A small plug of cotton should be placed below the stopper to prevent dust from the calcium chloride being carried out mechanically. Short caps of rubber tubing fitting the ends of the U-tube closely and closed with glass rods should be provided to protect the tube from the air when not in use and similar caps, also, for the potash bulbs. The caps must not contain loose sulphur. When great accuracy is desired, concentrated sulphuric acid is a more perfect drying agent than calcium chloride. See Benedict, Am. Chem. J., 23, 326.

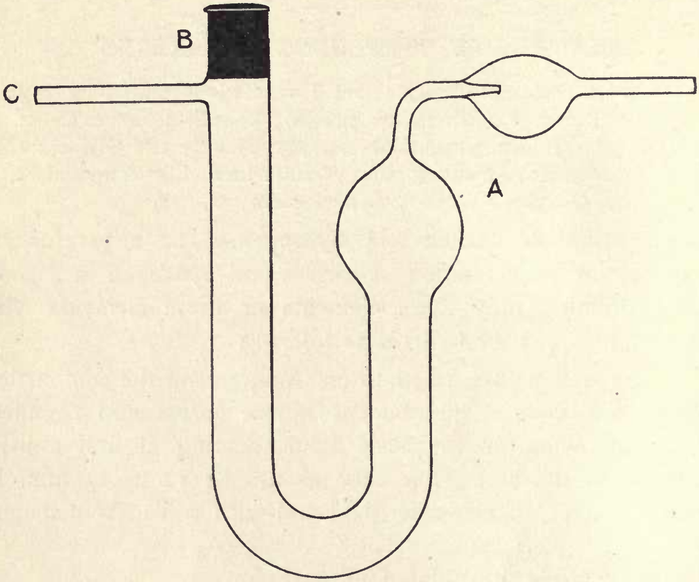

Fig. 1.

5. Potash bulbs, best of the improved Geissler form, having diaphragms within each bulb, also having a small tube to be filled

with granular stick potash "ground on." Instead of potash

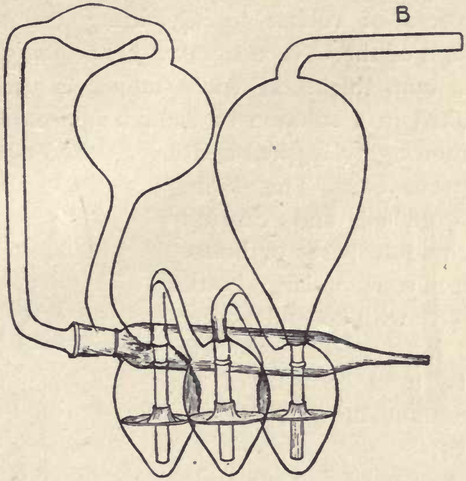

Fig. 2.

bulbs many chemists prefer a U-tube filled with soda-lime. (Benedict: Am. Chem. J., 23, 323 and 334.) The portion of the U-tube on the side where the gases leave the tube should be filled with calcium chloride for 3 to 4 cm., or a second tube containing glass wool and a little sulphuric acid may be used and weighed with the soda-lime tube.

If potash bulbs are used, they are filled with a solution of potassium hydroxide of about 1.27 sp. gr. prepared by dissolving 35 grams of potassium hydroxide in 100 cc. of water. Only enough of the solution should be used so that the three lower bulbs are filled and a very little passes into the fourth bulb when air is passed through the system. After filling, the tube B, through which the solution is drawn, it should be carefully cleaned both within and without before putting on the rubber caps. It is safer to use the bulbs only twice before refilling and in no case should they be used after acid potassium carbonate separates in the first bulb.

6. A small calcium chloride tube and a piece of rubber tubing to connect it with the potash tube of the potash bulbs.

7. Short pieces of rubber tubing fitting the tubes of the potash bulbs and of the U-tube tightly. The tubing should have walls about 2 mm. thick. If white tubing is used, the tubes should be soaked in a solution of sodium hydroxide to remove sulphur and thoroughly washed and dried. Red or black tubing is usually preferred, The tubing should be stretched and carefully examined for minute pores or holes.

8. Two gasometers or large bottles filled respectively with air and oxygen. A galvanized iron or zinc gasometer should not be used because of the danger of contaminating the gases with hydrogen.

9. Two sets of purifying apparatus to remove carbon dioxide and moisture from the air and oxygen. A suitable form is shown in Fig. 3. The space around the inner tube is filled with soda-lime and the inner tube, which passes loosely through a larger tube that separates it from the soda-lime, is filled with pumice drenched with concentrated sulphuric acid (Benedict, Am. Chem, J., 23, 332). If calcium chloride is used to absorb the water from the combustion, it should be used last in the purifying train, while if sulphuric acid is used for the former, it should be used last in the the purifying train, also. Calcium chloride leaves 1.0 mg. of water in one liter of a gas dried by it at 15°, 1.5 mg. at 20°, 2.5 mg. at 25°, and 3.3 mg. at 30°, while concentrated sulphuric acid leaves only about 0.002 mg. per liter at 15° to 19°.

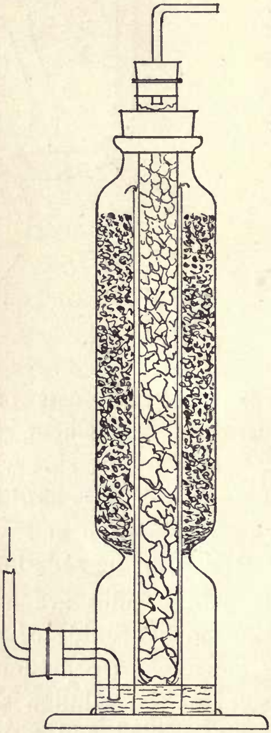

Fig. 3.

The connections from the gasometer to the combustion tube should be of glass, as far as possible with only short connections of rubber tubing, the glass tubes being brought together within the rubber. Moisture and other gases diffuse through india rubber, and there is some danger of organic matter being volatilized from the interior of a long rubber tube.

Between the purifying apparatus and the combustion tube a three-way stop-cock is introduced so that either air or oxygen may be passed through the tube at will and so that the rate of either current may be accurately regulated.

10. A porcelain or platinum boat, or, for volatile substances, a small bulb to contain the substance to be burned. Liquids which boil above 250° at atmospheric pressure may be weighed in a boat, but should be weighed immediately before burning. If a bulb is used, it should have a not too narrow capillary stem, at least 10 cm. long and should contain a small piece of copper oxide to burn the portion of the vapor of the substances remaining in the bulb. The bulb is filled by means of a small tube drawn out to a fine capillary, which can be inserted through the capillary of the bulb. Or it may be filled by heating the bulb and dipping the capillary stem in the liquid, allowing the latter to be drawn up as the bulb cools. The bulb should, of course, have a capacity of only 0.3 to 0.5 cc. It should be placed in the combustion tube in such a manner that by heating the portion of the tube where the bulb rests, the liquid can be forced out into some of the copper oxide which is still cold. Without this precaution it is difficult to avoid too rapid combustion.

11. Rubber stoppers fitting the combustion tube, soft and of the best quality. It is well to soak them in a solution of sodium hydroxide for a short time to remove sulphur. They should, of course, be washed clean and be dry.

12. Two asbestos shields to place over the combustion tube at the ends of the furnace to protect the rubber stoppers.

The combustion tube is filled as shown in Fig. 4. If the copper oxide is to be used for the first time, the tube (without the reduced copper spiral) should be placed in the furnace and heated to bright redness in a slow current of air for an hour. If the copper oxide and tube have been used before, heating for half an hour will suffice. The portion of the tube where the substance is to be placed is then allowed to cool, while the entrance of moist air is prevented by connecting the exit end of the tube with a calcium chloride or soda-lime tube.

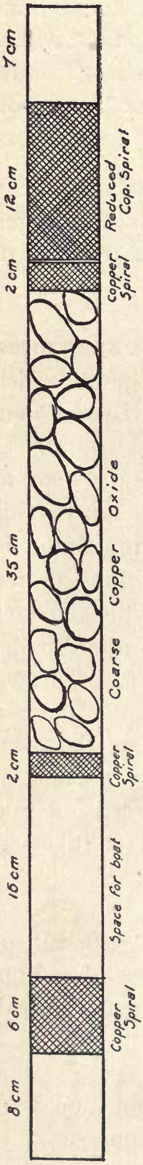

Fig. 4.

The potash bulbs and U-tube are carefully wiped with a clean dry cloth, and should be allowed to stand in or near the balance (with the caps on) for an hour before weighing.[1] They are weighed *without the caps.* The accuracy of the weighing may be increased by using a counterpoise of exactly the same character and kept beside the U-tube and potash bulbs during all of the operations. If proper care is taken and good common sense is used with regard to the conditions of weighing and methods of handling a reasonable degree of accuracy can be secured without this precaution.

When the combustion tube has cooled sufficiently, the reduced copper spiral is placed in the front part of the tube (if the substance to be analyzed contains nitrogen) and the rubber stopper carrying the calcium chloride U-tube is inserted and the potash bulbs connected to the U-tube and the calcium chloride or soda-lime tube connected to the exit of the potash bulbs to protect them from moisture and carbon dioxide

[1] A little radium in the balance case will dissipate electric charges which are sometimes troublesome (T. W. Richards).

from the air. In forcing the tube of the U-tube through the stopper and in making the connections the tube and bulbs should always be grasped by the small tube which is to be forced into the stopper or connection, as the apparatus is fragile. The glass tubes should be brought together within the connections and should be secured against leakage by tying with fine copper wire, thread or by a rubber thread made by breaking a rubber band. One of the greatest dangers of the whole process is that of slight leaks in the connections. After all of the connections are complete, a test for leaks may be made by admitting oxygen from the rear and after stopping the current, watching to see if the solution in the potash bulbs falls back from the level to which it is forced. The test is not always satisfactory, especially when a part of the tube is warm.

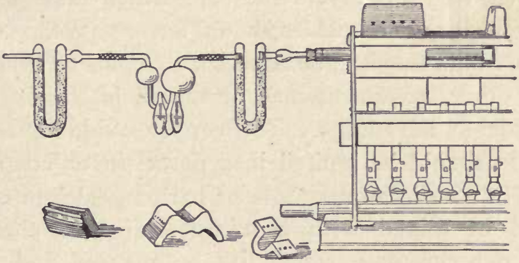

Fig. 5.

When the absorption train has been properly connected to the front end of the tube the stopper at the rear is removed, the oxidized copper spiral taken out and put into a *dry* test tube, which is immediately stoppered, the boat or bulb containing 0.15 to 0.25 grams of the substance introduced and the oxidized spiral replaced with the least possible exposure to the air, since copper oxide is hygroscopic. The rear stopper connecting with the purifying trains for oxygen and air is then inserted and the test for leaks referred to above, is made.

If no leak is found, light the first six or seven burners and turn them very low, either individually, or by means of the stop-cock regulating the gas supply for the whole furnace.

Turn these burners up a little once in two minutes, by the watch, till the front portion of the tube shows faint redness, then proceed slowly with the burners further back toward the substance. At the same time light one burner under the spiral in the rear of the boat or bulb, and start a very slow current of oxygen through the tube. The portion of the tube in the neighborhood of the boat must be heated *very gradually* in all cases so that the substance is slowly volatilized and burned.

In the Berlin laboratory a clock-work device has been arranged to move some burners very slowly under the substance and secure slow and uniform burning. A porcelain boat with twelve compartments is used to hold the substance.

Substances vary greatly in the care which must be exercised in burning them. The bubbles should never pass the potash bulbs more rapidly than they can be counted. Explosive substances and sometimes other substances may be mixed in the boat with fine copper oxide to advantage. The copper oxide to be used for this purpose should be ignited in a porcelain or copper crucible and cooled in a desiccator. Salts of barium, calcium or the alkalies should be mixed with a mixture of lead chromate and potassium pyrochromate which has been fused and pulverized. This will decompose the metallic carbonate formed and expel the carbon dioxide.

When the combustion of the substance is nearly finished the current of gas passing into the potash bulbs will usually slaken and the portion of the tube containing the boat may be brought to full redness while the current of oxygen may be considerably increased as the reduced copper is being reoxidized. At the same time the flames under the reduced copper spiral should be lowered to prevent undue oxidation of the latter. Water sometimes condenses in the front end of the combustion tube. This may be driven on into the calcium chloride tube by very careful warming with a flame or by holding a hot tile from the furnace near the tube. The current of oxygen is continued till it can be detected with a glowing splinter at the end of the protecting calcium chloride tube. It must then be displaced by dry air from the second gasometer, to avoid the error which would result if the calcium chloride tube and potash bulbs were weighed full of oxygen instead of air. The passage of 300 to 400 cc. of air will usually be enough. It is passed till a glowing splinter no longer shows oxygen at the exit. Not more than one-half liter to one liter of oxygen should be needed, if properly used. The use of excessive amounts of oxygen or air is to be avoided.

When the operation is complete the calcium chloride tube and potash bulbs are disconnected, protected at once with the rubber caps, wiped as before and placed near the balance for an hour before weighing.

The hydrogen is calculated from the weight of the water by the factor 0.1119, the carbon, most easily by taking 3/11 of the weight of the carbon dioxide.

For substances containing sulphur, lead chromate, fused and granulated, is used in place of copper oxide. For substances containing halogens a spiral of silver gauze or silver foil, heated only moderately, is inserted in place of the reduced copper spiral, or a boat containing reduced silver in the form of a powder may be used.

Determination of Nitrogen by the "Absolute" Method

Literature.—Johnson and Jenkins: Am. Chem. J., 2, 27; Schiff: Ber., 13, 885; Bradley and Hale: J. Am. Chem. Soc., 30, 1090.

For the determination of nitrogen by the absolute method the substance is burned in a current of carbon dioxide, the nitrogen is swept out into an azotometer filled with a solution of potassium hydroxide and the nitrogen is measured.

The combustion tube may be prepared in exactly the same manner (p. 6) as for the determination of oxygen and hydrogen,[1] though some prefer to seal the tube at the rear and put in that end a layer of magnesite 15 cm. in length, followed by a copper spiral, a layer of copper oxide, the substance mixed with copper oxide, a long layer of copper oxide and the reduced copper spiral.

---

[1] A tube used for nitrogen should not afterwards be used for carbon and hydrogen, unless it has been burned out in a current of oxygen.

If an open tube of the same form used for the determination of carbon and hydrogen is employed, the necessary carbon dioxide may be generated by heating about 25 grams of acid sodium carbonate in a hard glass tube protected by a sheet iron mantel. Between the generating tube and the combustion tube a small bulb tube of the form shown in Fig. 6 should be introduced to collect the water which comes from the acid carbonate.

The carbon dioxide may also be generated in the apparatus shown in Fig. 7. A is a 200 cc. Kjeldahl flask with a long neck. In it are placed 20 grams of acid sodium carbonate and 50 cc. of water. B is a separatory funnel having a long stem, all of it below C of capillary tubing, except the bulb at D, which has a capacity of 4-5 cc. This capillary tube should have an internal diameter of not more than 2 mm. The separatory funnel should contain 30 cc. of sulphuric acid (one part of concentrated acid to one of water by volume) which should be drawn into it through the capillary stem so that there will be no air below the stopcock. The capillary stem of the funnel should not dip below the surface of the solution and should be at least 30 cm. long to furnish enough pressure so that the gases can be readily forced through the combustion tube and into the azotometer. While the front portion of the combustion tube is being heated the solution in the generator is boiled very gently for about 10 minutes, causing a slow evolution of carbon dioxide, which will expel the air from the water and flask. The exit tube is then closed tightly with a short piece of rubber tubing and pinch-cock and the

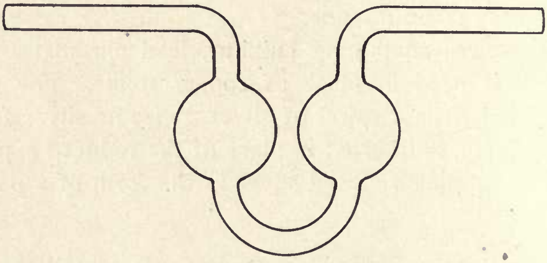
Fig. 6.

stop-cock of the separatory funnel opened very cautiously so that the acid may drop in *very slowly.* As soon as the apparatus is cooled a little the exit tube is connected with the bulb tube (Fig. 6) and the latter to the rear end of the combustion tube, into which the substance has meantime, been introduced in a boat or bulb, as described for the determination of carbon and hydrogen. The other end of the combustion tube is connected with the azotometer shown in Fig. 8. The mercury in the lower

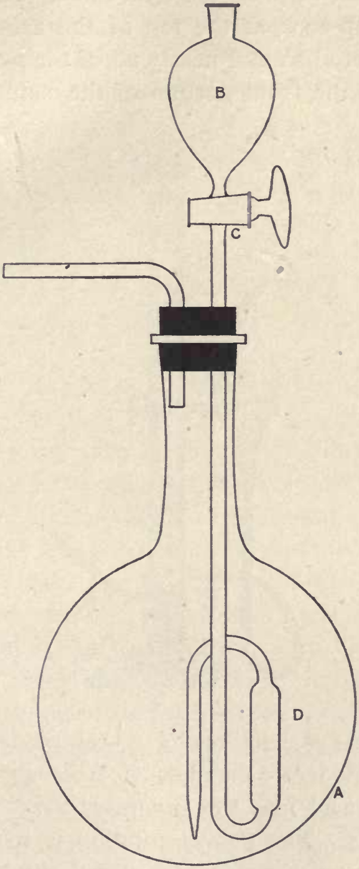

Fig. 7.

end of the azotometer should come about 1 cm. above the entrance of the side tube through which the gases are delivered. The potash solution is prepared by dissolving 100 grams of stick potash in 100 cc. of water giving a solution which contains approximately 40 per cent. of potasium hydroxide. At this point in the operation the stop-cock at the top of the azotometer is opened and the bulb lowered so that nearly all of the potash solution is in the bulb. While the front portion of the combustion tube is hot and after all of the connections have been made as described, the generation of a moderate current of carbon dioxide is continued by dropping the acid into the generator *very slowly* during ten or fifteen minutes. The potash solution is then brought to the top of the azotometer, the stop-cock closed, the bulb lowered again to reduce the pressure and the carbon dioxide entering the azotometer examined to see if it is free from air and completely absorbed by the potassium hydroxide. During this part of the operation great care must be taken that the substance does not become warm enough so that any of it volatilizes or decom-

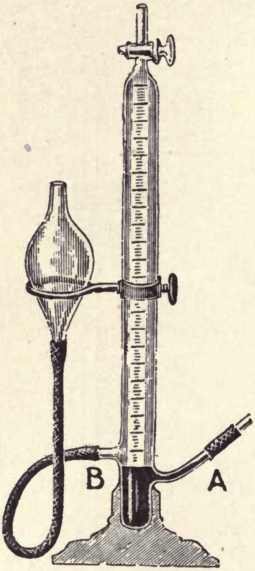

Fig. 8.

poses. If the test is satisfactory, then the combustion may be carried out essentially as in the determination of carbon and hydrogen. During the combustion the current of carbon dioxide should be very slow indeed. It is continued till the portion of the tube containing the substance has been heated to bright redness and no more nitrogen passes into the azotometer. After the combustion is completed the azotometer is placed in a room of uniform temperature and the volume of the nitrogen is read after half an hour or an hour. During this time the bulb connected with the side tube should be brought to the level of the top of the potash solution in the azotometer so that the gas will be under atmospheric pressure and less likely to change its volume by leakage. It hardly need be said that the stop-cock must be carefully lubricated with a viscous lubricant. It is also well to have a little of the potash solution in the tube above the stop-cock.

The azotometer should be carefully calibrated. This may be done by attaching to the lower end, at B, a rubber tube, pinchcock and delivery tip such as is used with a Mohr's burette. The first two or three cubic centimeters at the top should be calibrated with the burette filled with a potassium hydroxide solution of about the same strength as that used in the analysis, since the form of meniscus of such a solution is quite different from that of pure water. The specific gravity of the solution used must, of course, be known, accurately. For the rest of the azotometer pure water may be used for the calibration, since it is the value of the intervals between successive marks which is required. For the calculation of the volume from the weights of water see p. 33.

In reading the volume of the nitrogen the level of the potash solution in the bulb must be brought to the level of the top of the solution in the azotometer so that the nitrogen will be at atmospheric pressure. At the time of this reading the pressure of the air is determined by means of a barometer, whose reading should be corrected to zero.

For a pressure of 760 mm. the correction which is to be subtracted from the reading of the barometer is:

t°	Correction for glass scale	Correction for brass scale
5	0.7	0.6
10	1.3	1.2
15	2.0	1.9
20	2.7	2.5
25	3.3	3.1
30	4.0	3.7
35	4.7	4.3

A change of 7.6 mm. in the pressure causes a change of one per cent. in the correction. Thus if the pressure read is 730 mm. at 25° the correction is to be diminished by 4 per cent. and becomes 3.2 for a glass scale. This secondary correction is too small to be of practical importance for gases at atmospheric pressure.

The temperature is determined by means of a thermometer placed beside the azotometer.

The weight of the nitrogen may be calculated by the formula:

$$\text{Wt. in grams} = 0.0012507\ V \times \frac{(P-p)}{760} \times \frac{273\text{[1]}}{(273+t)}$$

$$= 0.00449\ V \times \frac{P-p}{273+t}$$

V = Volume in cubic centimeters
t = temperature of the gas
P = Barometric pressure
p = Aqueous pressure of a 40 per cent. solution of potassium hydroxide.

Table of Vapor Pressure

Aqueous pressure in millimeters of pure water and of a 40 per cent. solution of potassium hydroxide[2]

t°	Pure H_2O	40% KOH	t°	Pure H_2O	40% KOH	t°	Pure H_2O	40% KOH
0	4.6	2.6	12	10.5	5.8	24	22.2	11.7
1	4.9	2.8	13	11.2	6.1	25	23.5	12.4
2	5.3	3.0	14	11.9	6.5	26	25.0	13.1
3	5.7	3.2	15	12.7	6.9	27	26.5	13.6
4	6.1	3.4	16	13.6	7.4	28	28.1	14.7
5	6.5	3.6	17	14.4	7.8	29	29.8	15.5
6	7.0	3.9	18	15.4	8.3	30	31.6	16.4
7	7.5	4.1	19	16.4	8.9	31	33.4	17.3
8	8.0	4.4	20	17.4	9.3	32	35.4	18.3
9	8.6	4.7	21	18.5	9.9	33	37.4	18.4
10	9.2	5.1	22	19.7	10.5	34	39.6	20.5
11	9.8	5.4	23	20.9	11.1	35	41.9	21.5

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[1] The fraction $\frac{272}{272+t}$ would be more accurate, as nitrogen is not an ideal gas, but the error of the usual formula is only one part in 1300 at 25°.

[2] Prepared by interpolation from the Landolt-Bernstein-Meyerhoffer Tabellen, pp. 71 and 72a.

REDUCTION OF CUBIC CENTIMETERS OF NITROGEN TO GRAMS

Log. $\dfrac{0.0012507}{(1 + 0.003676)760}$ for each tenth of a degree from 0° to 35°[1]

t°	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	$\bar{6}$.21634	618	603	587	571	555	539	523	507	491
1	475	459	443	427	411	396	380	364	348	332
2	316	300	284	268	252	236	221	205	189	174
3	158	142	127	111	095	079	064	048	032	017
4	001	—986	—970	—954	—939	—923	—907	—892	—876	—860
5	$\bar{6}$.20844	829	813	798	782	767	751	735	719	703
6	687	672	656	641	625	609	594	578	563	547
7	531	516	500	484	469	453	437	422	406	391
8	375	360	344	329	313	298	282	267	251	236
9	221	205	190	174	159	143	128	112	097	082
10	066	051	035	020	005	—989	—974	—968	—943	—928
11	$\bar{6}$.19913	897	882	867	852	836	821	806	791	776
12	759	744	729	714	699	684	679	653	638	623
13	607	592	577	562	547	531	516	501	486	471
14	455	440	425	410	395	380	365	350	335	320
15	304	289	274	259	244	229	214	199	184	169
16	153	138	123	108	093	078	063	048	033	018
17	002	—987	—972	—957	—942	—927	—912	—897	—882	—867
18	$\bar{6}$.18852	837	822	807	792	777	762	747	732	717
19	703	688	673	658	643	628	613	598	583	568
20	553	538	523	508	493	478	464	449	434	419
21	405	390	375	360	345	331	316	301	286	271
22	257	242	227	213	198	183	168	154	139	124
23	109	095	080	066	051	036	021	007	—992	—977
24	$\bar{6}$.17962	947	932	918	903	888	874	859	845	830
25	816	801	786	772	757	742	728	713	699	684
26	670	655	641	626	612	597	583	568	554	539
27	524	510	496	481	467	452	438	423	409	394
28	379	364	350	335	321	306	292	278	263	249
29	235	220	206	191	177	163	148	134	119	105
30	091	077	063	048	034	020	005	—991	—977	—962
31	$\bar{6}$.16947	933	919	904	889	875	861	847	833	819
32	804	790	776	762	747	733	719	704	690	675
33	661	647	633	619	604	590	576	562	548	534
34	519	505	491	477	462	448	434	420	406	392

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[1] From Frankland's Water Analysis, corrected for the modern values for the weight and coefficient of expansion of nitrogen.

The accompanying table will be found more convenient for the calculations. Add together the logarithm corresponding to the temperature taken from the table, the logarithm of the volume and the logarithm of (P — p). The sum will be the logarithm of the weight of nitrogen in milligrams.

Weight of Nitrogen in One Cubic Centimeter of the Gas Measured over Water

If the gas is measured over a 40 per cent. solution of potassium hydroxide, add to the barometric reading the difference between the aqueous pressure of pure water and that of the potassium hydroxide solution at the given temperature. The table is based on 1.2507 as the weight of one cubic centimeter of dry nitrogen at 0° and 760 mm.

t°	721	724	727	730	733	736	739	742	745
10	1.130	1.135	1.139	1.144	1.149	1.154	1.158	1.163	1.168
11	1.125	1.129	1.134	1.139	1.144	1.148	1.153	1.158	1.162
12	1.120	1.124	1.129	1.134	1.139	1.143	1.148	1.153	1.157
13	1.115	1.119	1.124	1.129	1.134	1.138	1.143	1.148	1.152
14	1.110	1.114	1.119	1.124	1.129	1.133	1.138	1.143	1.147
15	1.105	1.109	1.114	1.119	1.124	1.128	1.133	1.138	1.142
16	1.099	1.103	1.208	1.113	1.118	1.123	1.127	1.132	1.137
17	1.094	1.098	1.203	1.108	1.113	1.118	1.123	1.128	1.132
18	1.089	1.093	1.098	1.102	1.107	1.112	1.116	1.121	1.125
19	1.084	1.088	1.093	1.097	1.102	1.107	1.111	1.116	1.120
20	1.079	1.083	1.088	1.092	1.097	1.102	1.106	1.111	1.115
21	1.074	1.078	1.082	1.087	1.091	1.096	1.101	1.106	1.110
22	1.068	1.072	1.076	1.081	1.086	1.091	1.095	1.100	1.104
23	1.062	1.067	1.071	1.076	1.080	1.085	1.090	1.094	1.098
24	1.057	1.061	1.066	1.071	1.075	1.080	1.084	1.089	1.093
25	1.051	1.056	1.060	1.065	1.069	1.074	1.078	1.083	1.087
26	1.056	1.050	1.054	1.059	1.064	1.068	1.072	1.077	1.082
27	1.040	1.044	1.048	1.053	1.058	1.062	1.066	1.071	1.076
28	1.034	1.038	1.042	1.047	1.052	1.056	1.060	1.065	1.070
29	1.028	1.032	1.036	1.041	1.046	1.050	1.054	1.059	1.063
30	1.022	1.026	1.031	1.035	1.040	1.044	1.048	1.053	1.057
31	1.015	1.020	1.024	1.029	1.033	1.038	1.042	1.046	1.051
32	1.009	1.014	1.018	1.022	1.027	1.032	1.036	1.040	1.044
33	1.003	1.008	1.012	1.016	1.021	1.026	1.030	1.034	1.038
34	0.996	1.001	1.005	1.009	1.014	1.019	1.023	1.027	1.031
35	0.990	0.995	0.999	1.003	1.008	1.012	1.017	1.021	1.025

WEIGHT OF NITROGEN IN ONE CUBIC CENTIMETER OF THE GAS MEASURED OVER WATER—(*Continued*)

t°	748	751	754	757	760	763	766	769	772
10	1.173	1.177	1.182	1.187	1.192	1.197	1.202	1.206	1.211
11	1.167	1.172	1.176	1.181	1.186	1.191	1.196	1.200	1.205
12	1.162	1.167	1.171	1.176	1.181	1.186	1.190	1.195	1.199
13	1.157	1.162	1.166	1.171	1.176	1.181	1.185	1.190	1.194
14	1.152	1.157	1.161	1.166	1.171	1.176	1.180	1.185	1.189
15	1.147	1.152	1.156	1.161	1.166	1.170	1.175	1.180	1.184
16	1.141	1.146	1.150	1.155	1.160	1.164	1.169	1.174	1.178
17	1.136	1.140	1.144	1.149	1.154	1.158	1.163	1.167	1.172
18	1.130	1.135	1.139	1.144	1.149	1.153	1.158	1.162	1.167
19	1.125	1.130	1.134	1.139	1.144	1.148	1.153	1.157	1.162
20	1.120	1.125	1.129	1.134	1.138	1.143	1.148	1.152	1.157
21	1.114	1.119	1.123	1.128	1.133	1.138	1.142	1.147	1.151
22	1.108	1.113	1.118	1.123	1.127	1.132	1.136	1.141	1.145
23	1.103	1.107	1.111	1.116	1.121	1.126	1.131	1.136	1.140
24	1.097	1.101	1.106	1.111	1.116	1.121	1.125	1.130	1.134
25	1.092	1.096	1.101	1.105	1.110	1.115	1.119	1.124	1.129
26	1.086	1.090	1.095	1.099	1.104	1.108	1.113	1.117	1.122
27	1.080	1.084	1.089	1.093	1.098	1.102	1.107	1.111	1.116
28	1.074	1.078	1.083	1.087	1.092	1.096	1.101	1.105	1.110
29	1.068	1.072	1.077	1.081	1.086	1.090	1.095	1.099	1.104
30	1.062	1.066	1.971	1.075	1.080	1.084	1.089	1.093	1.098
31	1.056	1.060	1.064	1.069	1.073	1.078	1.082	1.087	1.092
32	1.049	1.053	1.158	1.062	1.066	1.071	1.076	1.080	1.085
33	1.043	1.047	1.051	1.055	1.059	1.064	1.069	1.074	1.079
34	1.036	1.040	1.044	1.049	1.053	1.058	1.063	1.067	1.072
35	1.030	1.034	1.038	1.043	1.047	1.051	1.056	1.060	1.065

Not quite so accurate but still sufficiently so far all ordinary purposes is the table giving the weight of nitrogen in one cubic centimeter of the gas measured over water at different temperatures and pressures. The table may also be used for nitrogen measured over a solution of potassium hydroxide but for this purpose there must be added to the observed barometric pressure the difference between the pressure of water vapor for pure water and for the given solution. Thus the weight of the nitrogen in one cubic centimeter of the gas measured over 40 per cent. solution of potassium hydroxide at 25° and 751 mm. barometric pressure is 1.113 mg. while if measured over pure water it is 1.096. The error of calculation in using this table will not, in most cases, exceed one part in 1,000. The values obtained by means of some similar tables in common use are about one part in 250 too high, because the tables are based on the old, erroneous value for the weight of one cubic centimeter of nitrogen.

Determination of Nitrogen by the Kjeldahl Method

Literature.—Kjeldahl: Z. anal. Chem., 22, 366; Gunning: *Ibid,* 28, 188; Foerster: *Ibid,* 28, 422; Kober: J. Am. Chem. Soc., 30, 1131; Gill and Grindley: *Ibid,* 31, 1249; Kober: *Ibid,* 32, 689.

The nitrogen of amides, amines, proteins and of some other compounds may be determined by the Kjeldahl method, which consists in digesting the substance with hot, concentrated sulphuric acid, usually with the addition of some substance to aid in the oxidation, followed by dilution, neutralization and distillation of the ammonia from the alkaline solution. The nitrogen of nitro compounds and of nitrates may be determined by the same method, after previous reduction.

Place in a 300 cc., long necked, Kjeldahl flask, best of Jena glass, 0.2 to 0.5 gram of the substance to be analyzed, add 20 cc. of pure concentrated sulphuric acid, 10 grams of potassium sulphate and 0.5 gram of mercury.[1] The mercury is best measured in a very small capillary tube, having a mark on it to indicate the quantity which should be taken. Support the flask at an angle of 45° and heat the contents over a low flame, applied directly to the glass, for one to two hours. The contents of the flask should boil gently but not so rapidly that much sulphuric acid escapes from the mouth of the flask. The operation must, of course, be carried on in a hood with a good draft. If the contents of the flask does not become colorless at the end of two hours, the oxidation may be finished by adding carefully a small amount of potassium permanganate.

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[1] Some chemists use 0.1 gram of crystallized copper sulphate instead of mercury. In that case the subsequent use of potassium sulphide is not necessary.

Measure into a 300 cc. Erlenmeyer flask an amount of N/10 hydrochloric acid about ten per cent. in excess of that required to neutralize the ammonia expected from the quantity of substance taken. (1 cc. of N/10 hydrochloric acid is equivalent to 1.4 mg. N). Arrange a distilling apparatus as shown in the figure, the connection with the Kjeldahl flask being made by means of a Hopkins distilling bulb. The condenser tube is best of tin or aluminum. The bulb tube connected to the lower end of the condenser should dip under the surface of the standard acid. When the contents of the digestion flask is cooled sufficiently, add 150 cc. of water and cool again, then pour carefully down the side of the flask, so that it will run to the bottom without mixing, 80 cc. of a solution containing 30 grams of sodium hydroxide and 2 grams of potassium sulphide. Add two or three pieces of granulated zinc. Connect at once with

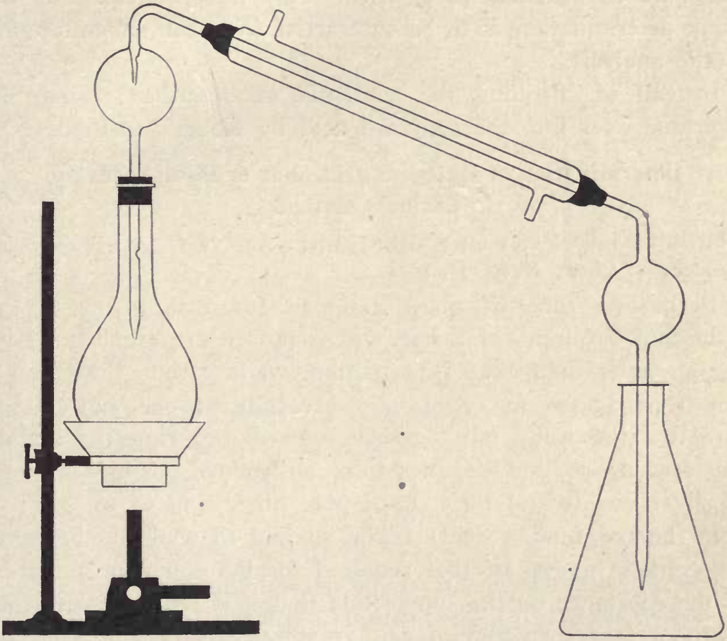

Fig. 9.

the distilling tube, mix the contents of the flask by careful shaking and distil over 125-150 cc. Titrate the excess of acid with standard alkali, using methyl orange or congo red or methyl red as indicator.

A blank experiment should be carried out with the same quantities of all the reagents, except that only 1 to 2 cc. of the standard acid should be used. Any nitrogen found in the blank determination is to be subtracted from the amount found in the analysis.

Instead of distilling the ammonia as described it may be aspirated over into the standard acid by Kober's method.

Determination of Halogens, Sulphur or Phosphorus by Carius's Method

Literature.—Carius: Ber., 3, 697; Küster: Ann., 285, 340; Walker and Henderson: Chem, News, 71, 103.

Prepare a tube of glass designed for sealing tubes (the "Einschmelzröhren" of Schott and Genossen are excellent) having an inner diameter of 14-16 mm. walls 2 mm. thick and a length of 35-40 cm. Seal very carefully at one end, taking care that the walls fall together somewhat during the sealing and that no portion becomes thin. Introduce one-half a gram of silver nitrate and 1-1.5 cc. of pure nitric acid of sp. gr. 1.50 (not the red fuming acid). The amount of acid should be 20 per cent. in excess of that required for the complete oxidation of the substance on the supposition that it is reduced to nitrous acid. A larger amount of acid is not necessary and increases the danger of explosion. Introduce the substance, weighed in a small tube, 2-3 cm. long and 6-8 mm. in diameter. Seal the other end of the tube carefully, drawing it out very slowly to prevent the wall from becoming thin at any point and having at the end a capillary tip 4-6 cm. long and with an internal diameter near the end of ½ mm. or less. Place the tube in a bomb furnace, raise the temperature slowly to 320° and keep it at 310°-330° for two hours. It need hardly be said that the furnace must be so placed with the ends protected by iron or heavy wooden shields that no one can be injured in case of an explosion. Where the furnace is thoroughly cold, remove the tube *very carefully* always keeping several thicknesses of a towel or heavy cloth between the tube and the hand or body and wrapping it well in a towel as soon as it is removed from the furnace. A better method, which should always be used when possible, is to have a furnace with movable iron tubes and to keep the sealed tube almost entirely in the iron tube until the pressure has been relieved by holding the tip in the flame of a burner till the internal pressure has blown out an opening. During this operation the tube is held with the end bearing the capillary tip high enough so that the contents of the tube will run to the lower end. The eyes should be protected by goggles. After the pressure has been relieved the end of the tube is cut off and the silver halide is carefully rinsed out into a small beaker. If some of the silver halide can not be removed from the tube by rinsing, it may be dissolved in a very little ammonia and the solution added to the contents of the beaker. In such a case the solution in the beaker must stand in the dark till the precipitate has settled before filtering. In the case of silver iodide or bromide it is advisable to digest the solution and precipitate on the water-bath for a short time to decompose double compounds which are formed with the excess of silver nitrate. The solution is filtered on a Gooch crucible, the precipitate washed and finally dried at 150°-200°.

For the determination of sulphur or phosphorus the addition of silver nitrate is omitted and the sulphuric or phosphoric acid in the diluted oxidation mixture is determined by the usual analytical methods with use of barium chloride or molybdic mixture.

Determination of Halogens or Sulphur by Pringsheim's Method

Literature.—Pringsheim: Am. Chem. J., 31, 386; Ber., 36, 4244; Schreiber: J. Am. Chem. Soc., 32, 977.

About 0.2 gram of the substance is mixed with sodium peroxide in a brass or steel crucible of the form shown in Fig. 10. If the substance contains 75 per cent. of carbon and hydrogen.

18 times its weight of the peroxide should be used. If it contains 50 to 75 per cent. of carbon and hydrogen, 16 times its weight should be used; if it contains 25 to 50 per cent. it should be mixed with half of its weight of sugar and if it contains less than 25 per cent. it should be mixed with an equal weight of sugar, the amount of peroxide being in the former case 16 times and in the latter case 18 times the weight of the mixture. For practically all cases a stock mixture of one part of sugar with 25 parts of sodium peroxide may be prepared and one part of the substance to be burned mixed with 30-32 parts of this

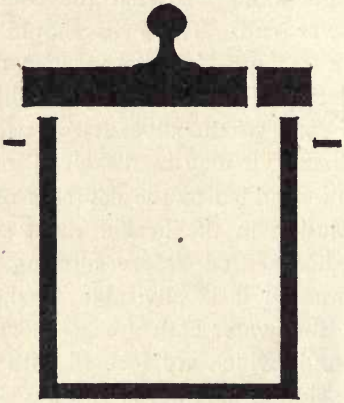

Fig. 10.

mixture. The sugar and substance must be finely powdered, the latter, of course, before weighing. They are intimately mixed with the sodium peroxide in the crucible by means of a small nail, which is left in the crucible during the ignition. The cover is placed on the crucible and the latter is immersed in distilled water in a porcelain dish to within 3 or 4 mm. of its upper edge. The mixture is ignited by thrusting a red hot iron wire through the hole in the lid. If the mixture ignites very rapidly with the evolution of considerable gas, and smoke and flame appear through the nail hole in the lid, too much carbonaceous matter has been used. If the mixture fails to ignite throughout, too much sodium peroxide has been taken. In either case it is best to repeat the ignition, though, if the sample is valuable it can be saved in the second case by completing the ignition over the blast. When the reaction is complete, the crucible is turned on its side and the contents of the dish warmed gently till solution is complete. The solution is then filtered, 5 cc. of a strong solution of sodium sulphite added to reduce any oxygen acids of the halogens which may have been formed, and then dilute sulphuric acid to strongly acid reaction. The halogen acid may be precipitated in the usual manner with silver nitrate or it may be titrated by Volhard's method. In the latter case an excess of silver nitrate should be added either before or immediately after acidifying and the solution boiled to expel sulphur dioxide before titrating back with the thiocyanate. Also, if chlorine is to be determined, the silver chloride must be filtered off before titrating (Rosanoff and Hill: J. Am. Chem. Soc., 29, 269). Sulphur and phosphorus may also be determined by burning the substance with sodium peroxide followed by precipitation from the acidified solution. The method is not adapted for use with liquids.

Determination of Halogens by Reduction with Sodium and Absolute Alcohol

Literature.—Stepanow: Ber., 39, 4056; Bacon: J. Am. Chem. Soc., 31, 49.

For liquid substances and substances which ignite on mixing with sodium peroxide the method of Stepanow is very suitable. Introduce into 150 cc. Kjeldahl flask 0.2 gram of the substance to be analyzed and 35 cc. of absolute alcohol (98 per cent. at least) if it contains chlorine, 18 cc. if it contains bromine or 13 cc. if it contains iodine. Connect the flask with an upright condenser, support it on a thin sheet of asbestos on a wire gauze, warm gently till the substance is dissolved and add gradually, during at least 30 minutes, through the condenser, 3.5, 1.7, or 1.1 grams of sodium according as the substance contains chlorine, bromine or iodine. Toward the end keep the solution boiling gently with a burner and boil the solution for one hour after the sodium is all dissolved. Allow the solution to cool to 50° or 60°, add, cautiously, 50 cc. of water through the condenser, cool, acidify with nitric acid, add an excess of standard silver nitrate, filter, if the halide is chlorine (Rosanoff and Hill: J. Am. Chem. Soc., 29, 269), add ferric sulphate and titrate with a standard solution of ammonium thiocyanate by Volhard's method.

Determination of Barium, Strontium, or Calcium in Salts of Organic Acids.—Weigh 0.2 to 0.3 gram of the salt in a platinum crucible and heat in an air-bath for 1 to 2 hours at 100° to 200° according to the nature of the salt. In the case of salts of unknown properties, it is safest to dry to constant weight in a vacuum desiccator first, then successively at 100°, 135°, 175° and 200°, noting at which temperature a constant weight can be obtained without decomposition. After determining, as above, water of hydration, if present, add to the salt one or two drops of concentrated sulphuric acid and heat very gently over a low flame till fumes of sulphuric acid cease to escape, then at faint redness till the sulphate formed is pure white. Cool and weigh, then moisten with a drop of concentrated sulphuric acid and heat very gently till the acid is expelled and finally again to faint redness. If the contents of the crucible increases in weight, the presence of a little sulphide at the end of the first heating is indicated and the second weight is to be taken. In calcium salts the metal may be determined as calcium oxide by direct ignition over the blast lamp.

Determination of Sodium, Potassium or Other Metals.—Sodium and potassium may be determined as sulphates by ignition with sulphuric acid as described above but the temperature of the crucible must never be above dull redness for fear of volatilizing some of the salt. Also. after the salt is pure white, some solid ammonium carbonate should be thrown into the crucible several times and the heating continued to convert any acid sulphate present into the neutral salt.

In silver salts the silver may be determined as metallic silver by gentle ignition in a porcelain crucible.

Chapter II

GENERAL OPERATIONS

The most important general operations used in the preparation of pure substances are separation by means of solvents, extraction with ether or other immiscible solvents (p. 167, 54); crystallization (p. 129), fractional crystallization (p. 122), fractional distillation, distillation under diminished pressure (p. 172), distillation with steam (p. 71), sublimation (p. 80), filtration (p. 120), and determination of the melting-point, boiling-point and specific gravity. In this chapter only fractional distillation, the determination of the boiling-point, the determination of the melting-point and the determination of specific gravity will be considered. The other operations will be discussed in connection with preparations in which they are used.

At the close of the chapter directions for the distillation of wood and separation of the various products formed are given as an illustration of a number of operations common both in the laboratory and in technical processes.

1. Fractional Distillation and the Determination of Boiling-points.—Carbon tetrachloride and aniline.

Literature.—Theory of fractional distillation; Nernst: Theoretische Chemie, 6th Edition, p. 111; Noyes: Organic Chemistry, p. 13; Correction of thermometers; Crafts: Am. Chem. J., **5**, 324; Circular of the Bureau of Standards Washington; Rimbach: Ber., **22**, 3072; Apparatus for fractional condensation; Hahn: Ber., **43**, 419; C. A., **1910**, 1168; Prevention of bumping, Scudder: J. Am. Chem. Soc., **25**, 163; H. Meyer: Analyse und Konstitutionsermittelung org. Verbindungen, **2**, Aufl. pp. 46-47; Determination of boiling-point of a small amount of substance; Mulliken: A Method for the Identification of Pure Organic Substances, p. 222; Alex. Smith and Menzies: J. Am. Chem. Soc., **32**, 897; See also p. 269.

25 grams aniline.
25 grams carbon tetrachloride.

Place 25 grams of carbon tetrachloride in a 50 cc. flask containing 5 grams of powdered calcium chloride. In a second flask of the same size place 25 grams of aniline with 5 grams of powdered potassium hydroxide. After an hour, or better after standing over night, filter one of the liquids through a dry filter into a 50 cc. distilling bulb and distil slowly with the apparatus shown in the figure. The thermometer is held in place by a tightly fitting, sound and carefully bored cork, not a rubber stopper. It is usually best to make the hole with a cork-borer a little smaller than the thermometer and enlarge it by means of a round file. The bulb of the thermometer must always be placed a little below the side tube of the distilling bulb but should never be placed within the liquid or too close to it. The condensing tube for the present case may be about 1 cm. in internal diameter and 60 cm. long. For more volatile liquids than carbon tetrachloride or for the rapid distillation of larger amounts of substance a Liebig's condenser should be used. The condensing tube may be drawn out at the upper end so that the side tube of the distilling bulb will just enter it and connected with the latter by slipping a tightly fitting rubber tube over both. The distilling bulb is to be heated over a low flame applied directly to the bulb. A micro burner, if available, is most satisfactory for the purpose when a small quantity of liquid is to be distilled. Collect the first portion of the distillate in a dry test tube till the thermometer indicates a temperature within 1° of the boiling-

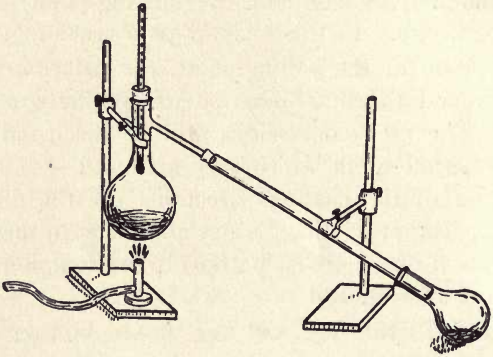

Fig. 11.

point (76.7° for carbon tetrachloride, 183.7° for aniline), then collect the principal portion, which should boil within an interval of two degrees, in a small *dry,* weighed flask.

A small additional amount, boiling within the proper interval may usually be obtained by redistilling the portions collected below and above the interval chosen.

Having determined the weights[1] of carbon tetrachloride and aniline obtained, mix them together and subject the mixture to fractional distillation collecting the successive fractions in a series of dry flasks or, for the smaller fractions, of test-tubes, labelling each with a gummed label marked with a pencil, or with a pencil which will write on glass. Eight or ten fractions should be collected, the temperature intervals being chosen with reference to the amounts of the distillates at different temperatures. The use of good common sense as to the amount which should be collected in each fraction and the corresponding temperature intervals to be chosen is one of the most important points in fractional distillation. In general, the fractions should be larger, and the temperature intervals also shorter, at points near the boiling-points of the substances to be separated.

When the whole has been distilled the apparatus is carefully cleaned and dried and the lowest boiling fraction returned to the bulb. This is then distilled and the first distillate collected in the same flask but for a much narrower interval of temperature than before, a second portion being collected in a new receptacle. When the lower temperature for the second fraction from the first distillation is approached that is added to the bulb through a small, dry, funnel, and the distillation continued, the distillate being collected, of course, in the proper flask or tube corresponding to the boiling-point. While the intervals of temperature in the neighborhood of the boiling-points of carbon tetrachloride and of the aniline should be shorter on the second distillation the intervals between may be lengthened, so that the total number of fractions is not increased. If a considerable portion is obtained boiling within an interval of two degrees of the boiling-points of carbon tetrachloride and aniline respectively, those fractions need not be distilled again but the intermediate fractions may be distilled once more to increase the amounts of these two principal fractions. Weigh these two fractions and determine the percentage yield.

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[1] Weigh roughly within 0.1 to 0.2 gram.

The slow distillation, which the air condenser makes necessary to avoid loss of carbon tetrachloride, conduces to a better separation, and, in general, distillation should not be conducted too rapidly in fractioning. A general rule is that the liquid should drop from the end of the condenser at the rate of two drops a second. The neck of the flask should always be placed over the end of the condensing tube to prevent loss by evaporation. With volatile or hygroscopic liquids the space between the condensing tube and the neck of the flask should be closed with cotton or with a cork having a V shaped piece cut from its side to allow escape of air.

When substances differing but little in their boiling-points are to be separated a Laenburg distilling bulb (p. 172) a Hempel tube filled with glass beads (p. 36) or a Hahn fractioning head (*loc. cit.*) may be used to advantage.

If the thread of the thermometer is not entirely immersed in the vapor, a correction must be added to its reading. This may be taken from Rimbach's table or calculated by the formula:

$\text{Cor.} = + \text{N}(t - t')0.000154.$

N = Number of degrees on the stem of the thermometer below the temperature read.

t = temperature read.

t' = Average temperature of the stem.

0.000154 = Coefficient of apparent expansion of mercury in glass.

The thermometer must also be tested to determine if it registers correctly. This is best done by means of the boiling-point of some pure substance which boils near the boiling-point to be determined. Suitable substances for this purpose are:

Ethyl ether	34.6°
Water	100 °
Ethylene bromide	130.3°
Aniline	183.7°
Naphthalene	218.1°
Benzophenone	306.1°

For the last two the boiling-points under varying pressures have been accurately determined. Crafts: Am. Chem. J., **5**, 324.

In case the pressure of the air is greater or less than 760 mm. a correction must be applied. For liquids which do not associate, when the pressure is not far from 760 mm. the correction for a difference of 10 mm. in the pressure may be found by dividing the absolute temperature of the boiling-point by 850. For associative liquids, as alcohols, acids and hydroxyl compounds generally, the factor is 1020. (Alex. Smith and Menzies: J. Am. Ch. Soc., **32**, 907.) The following table calculated on this basis will be found convenient.

Boiling-point (Ordinary scale)	Correction for a difference of 10 mm. in the pressure	
	For non-associating liquids	For alcohols, acids, etc.
50°	0.38°	0.32°
100°	0.44°	0.37°
150°	0.50°	0.42°
200°	0.56°	0.46°
250°	0.62°	0.51°
300°	0.68°	0.56°
350°	0.74°	0.61°
400°	0.80°	0.66°

By using a set of Anschütz thermometers, each of which has a range of only 60° to 70°, the correction for the stem may be made very small and usually may be neglected.

2. Determination of Melting-points.—Urea, phthalic anhydride, *p*-toluidine.

Literature.—Apparatus, Scudder: J. Am. Chem. Soc., **25**, 161; Thiele: Ber., **40**, 996; Correction for thermometers, Crafts: Amer. Chem. J., **5**, 324; Rimback: Ber., **22**, 3072.

The purity of solid substances is, in many cases, most easily tested by means of the melting-point. For this purpose the substance must be perfectly dry. The drying can be effected by allowing the body to lie for a sufficient length of time on filter-paper, or on clean, porous porcelain, best over sulphuric acid *in vacuo*.

A lot of capillary tubes for the determination of melting-points may be prepared by taking a soft glass tube with not too thin walls, 4 to 5 mm. in external diameter, and drawing it out as indicated above. (See Fig. 12.) The tube is then sealed off near each bulb, and the closed tubes kept till needed. For use, the bulb is cut in two by scratching with a file and breaking.[1] The finely powdered substance is put into the wide end of the tube and shaken down, or pushed down to the point with a clean platinum wire. For a melting-point bath the best for general use is a round-bottomed, 75 cc. flask, with a rather long neck. In the mouth is placed a stopper, perforated so that the thermometer will pass easily through it, and be held in place by a small wooden wedge, *e.g.*, a match stick. Through the side of the cork passes a small platinum wire with loops, as indicated in the figure. (See Fig. 13). If moistened with the sulphuric acid, the tube will adhere to the thermometer by capillary attraction, but such an arrangement is less secure. The part of the capillary tube containing the substance should lie in contact with the bulb of the thermometer. The bath may be heated rapidly with a free flame till the temperature approaches the melting-point, and then very slowly. In case of bodies which decompose at or near their melting-points, the thermometer and the tube should be brought as quickly as possible, without danger of breaking the thermometer, into the hot bath and the latter brought quickly to the melting-point. The result, in such cases, cannot be very accurate.

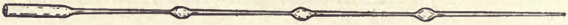

Fig. 12.

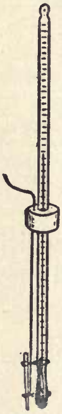

Fig. 13.

When, as is usually the case, the stem of the thermometer is not immersed in the sulphuric acid to the point to which the mercury rises, a correction similar to that for boiling-points must be applied. (See p. 28.)

In general, a sharp melting-point, within an interval of one degree, at most, is characteristic of a pure substance, while impure substances melt indefinitely.

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[1] Some chemists prefer thin, straight capillary tubes prepared by drawing out a test-tube. The tube should be about the size of the lead of a lead pencil.

Instead of the bulb, shown in Fig. 14, the Thiele apparatus

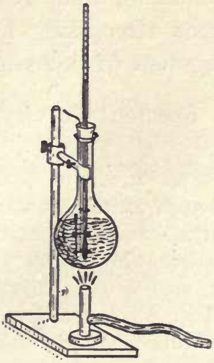

Fig. 14.

shown in Fig. 15 may be used to advantage. For temperatures be-

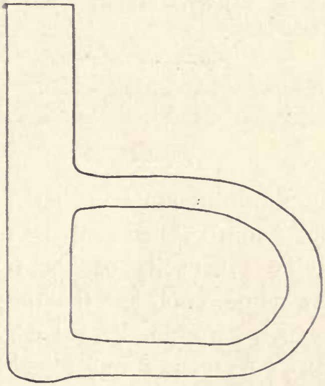

Fig. 15.

low 300° concentrated sulphuric acid may be used in the bulb or apparatus but a mixture of 7 parts of acid with 3 parts of potassium sulphate gives off less of acid vapors and may be heated to a higher temperature without boiling. A mixture of 6 parts of acid with 4 parts of potassium sulphate may be used to a temperature of 365° but becomes pasty or solid at ordinary temperatures. For still higher temperatures zinc chloride may be used but this must be poured into a shallow dish to solidify, as it expands on crystallizing and would burst the bulb. If the sulphuric acid darkens after using for some time, it may be cleared by adding a fragment of potassium nitrate.

3. Determination of Specific Gravity.—Specific gravity of alcohol.

Literature.—Circular No. 9, Bureau of Standards, Washington, Testing of Glass Volumetric Apparatus; Circular No. 16, Testing of Hydrometers; Circular No. 19, Standard Density and Volumetric Tables; Traube: Physikalisch-Chemische Methoden, pp. 12-24; Ostwald-Luther: Hand und Hilfsbuch zur ausführung Physiko-Chemischer Messungen, 2nd Edition, pp. 141; Morley: Alcoholometric Table, J. Am. Chem. Soc, **26,** 1185; A new, more accurate table will soon be issued by the Bureau of Standards.

Prepare a small bulb by drawing out a tube with a diameter of 1 cm. and wall about 1 mm. thick to the form shown in the Fig. 16. It should be drawn out in such a manner that the tube does not become too thin at A and that the internal diameter at that point is about 2 mm. Then seal the tube at B and form a flattened end leaving a capacity of about 1 cc. Anneal the bulb carefully in the flame, cool, cut the tube off about ½ cm. above the narrowest point, round the cut edge in the flame and make a narrow mark at A, using a moistened file, best moistened with a solution of camphor in turpentine. (A file moistened with this mixture will cut or bore glass rapidly.) Clean the bulb carefully with alcohol, introducing it and removing it with a tube drawn out to a capillary of such size that it will pass through the neck of the bulb. Warm the bulb gently and dry it by drawing air through it with the same capillary tube. Cool for half an hour in the balance case and weigh accurately. Fill the bulb with water to a point just above the mark, using the same tube as before. Bring the water in a 500 cc. beaker

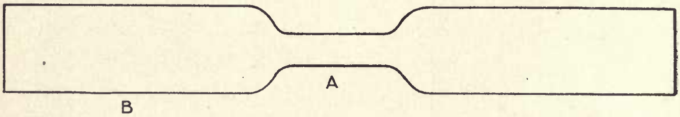

Fig. 16.

exactly to 20°. Place the bulb in the water, supporting it with a shelf so placed that the water comes to a point just below the neck of the bulb. After ten minutes bring the liquid in the bulb exactly to the mark by drawing out the excess with the capillary pipette. Wipe the bulb dry and weigh after half an hour. The weight of the water multiplied by 1.00282 will give the volume of the bulb in cubic centimeters.[1] The volume at 15° will be, for a capacity of 1 cc., 0.00012 cc. less and at 25° 0.00012 cc. more than at 20°, owing to the contraction or expansion of the glass. Remove the water, fill the bulb with alcohol, remove this and repeat twice, then dry as before. Fill the bulb with alcohol, set it in the beaker of water, and repeat the operations exactly as before. To the apparent weight of the alcohol there must be added 0.00109 gram for each cubic centimeter in the capacity of the bulb, to correct for the buoyancy of the air. The specific gravity referred to water at 4° will, of course, be the corrected weight of the alcohol divided by the volume, in cc., of the bulb.

It is always desirable to know the specific gravity of a new substance at two different temperatures. For this purpose the capacity of the bulb may be calculated at 15° and at 25° by the rule given above. The bulb may be filled with alcohol at 15° or 25° by keeping the water in the beaker at the desired temperature. To the apparent weight must be added 0.00111 gram at 15° or 0.00107 gram at 25° for each cc. as the correction to a vacuum.

Unless it is desired to determine the specific gravity to the fifth decimal, the value 0.0011 may be used for the corrrection at pressures above 750 mm. or 0.0010 at pressures of 700 to 750 mm.

A higher degree of accuracy may be obtained by the use of a larger pyknometer but this is useless unless the liquid examined is of a very high degree of purity. Determine the strength of the alcohol by weight and by volume with the use of Morley's table. (*loc. cit.*)

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[1] One gram of water at 20° fills a volume of 1.001768 cc. and one gram of water as indicated by brass weights is really 1.001053 gram, when corrected for the buoyancy of the air.

4. Distillation of Wood.

Literature.—J. Anal and Appl. Chem., 5, 241; Met. and Chem. Eng., 8, 155, 433. For acetone see also 33, p. 92.

1,200 grams of wood.

Put 1,200 grams of wood, cut into billets about an inch square into the iron retort shown in Fig. 17. The retort is of cast iron, 15 cm. inside diameter and 20 cm. deep, with walls 12 mm. thick. It is fitted with a thermometer, reaching well down into the charge of wood and with a glass delivery tube. Both the thermometer and delivery tube should pass through carefully bored, tightly fitting *cork* stoppers. The cover of the retort is held on with iron dogs and wedges, a thin sheet of asbestos being interposed between the cover and the body of the retort to insure a tight joint.[1] The retort is supported by a piece of thick asbestos board bent to the proper shape and held in place with wire. Openings are cut in the board above and below for the entry and exit of air and the retort is heated by a good triple burner.

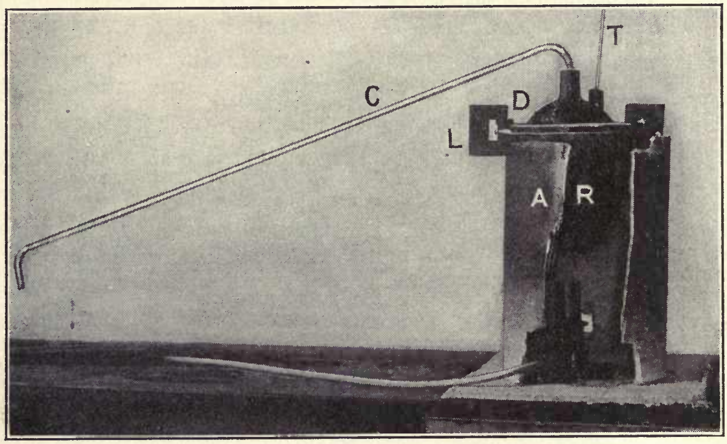

Fig. 17.

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[1] Instead of the retort described, the one shown in Fig. 17A may be used. This is 60 cm. long and 7.5 cm. in diameter, with walls about 6 mm. thick. There is a 2.5 cm. flange at the end ground smooth and fitted with a perforated iron plate attached as described above. The massive cast iron retort has proved more satisfactory.

Connect the delivery tube from the retort with a 750 cc. Erlenmeyer flask and the latter with a condenser and settling bottle (2½ liters) as shown in Fig. 18. The exit from the settling bottle is connected with a burner where the combustible gases are burned as they escape. When all is ready heat the retort

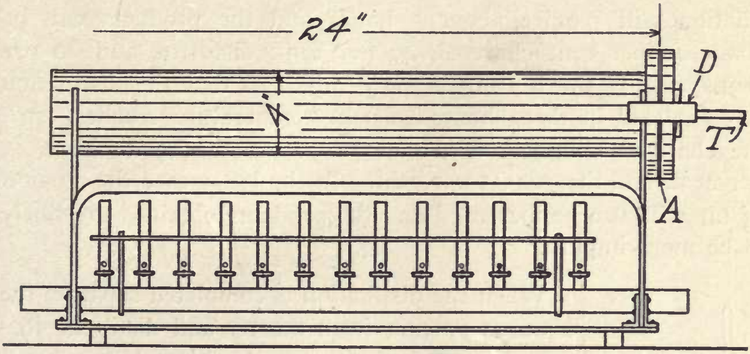
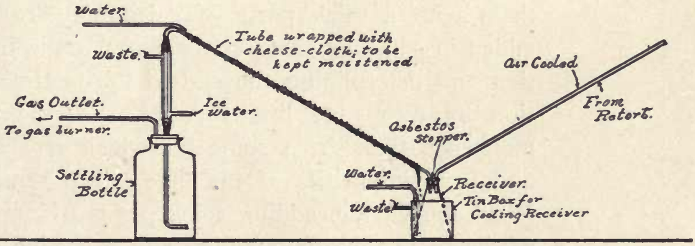


Fig. 17A.—Single tube retort, heated by gas, for the distillation of wood or calcium acetate. The whole apparatus is enclosed in a case of asbestos board to conserve the heat. The cover with the asbestos washer (A) is held in place by two dogs and wedges (D). The volatile products pass out from the retort through tube (T) to the condenser.


Water.
Waste.
Tube wrapped with cheese-cloth; to be kept moistened
Air Cooled
Gas Outlet.
To gas burner.
Ice Water.
From Retort.
Asbestos Stopper.
Settling Bottle
Water.
Receiver.
Waste.
Tin Box for Cooling Receiver

An Apparatus for collecting Distillate from Wood.

Fig. 18.

moderately so that toward the end of the distillation the thermometer goes to 210°-220°. Under these conditions the distillation will require about 5 hours and the products will be about 40 per cent charcoal, 40 per cent. distillate, and 20 per cent. gas. If the heating is more rapid, so that the distillation is completed in three hours and the temperature reaches 300°, the charcoal will be only about 30 per cent., the distillate 45 per cent. and the gas 25 per cent. In the latter case the amount of tar will also be increased and the products obtained are likely to be more impure.

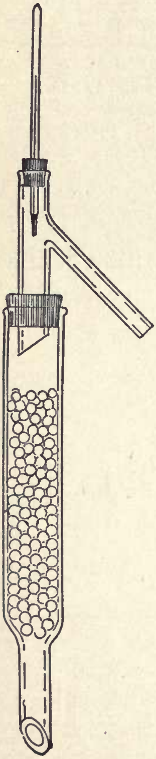


Fig. 18A.

When the distillation is completed separate the aqueous portion from the tar and distil the former from a flask connected with a Hempel column of glass beads (Fig. 18A). The tar is also heated to 140° in an oil-bath and any distillate obtained is mixed with the aqueous portion and distilled with that. Any oil which separates from the distillate is separated by means of a separatory funnel (p. 127). Repeat the distillation a second time to secure as complete a separation from the tar as possible. Unite the aqueous distillates in an Erlenmeyer flask and neutralize them with a thick paste of calcium hydroxide added in small portions, cooling after each addition and determining the end of the neutralization by means of litmus paper. Filter on a moistened filter from some tar which separates and from impurities of the lime which remain. Distil the filtrate, adding some pieces of porous porcelain to prevent bumping and collecting the distillate in three of four fractions, stopping the distillation when the temperature reaches 100°. Fractionate the distillate systematically to separate the methyl alcohol and acetone. The crude methyl alcohol may be freed from acetone by means of sodium hydrogen sulphite. The acetone may also be converted into the double compound with acid sodium sulphite (p. 92).

Evaporate the residue from which the methyl alcohol and acetone have been distilled and obtain from it ordinary gray calcium acetate.

Chapter III

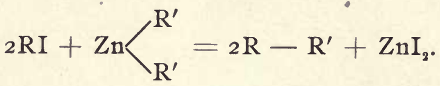
HYDROCARBONS

Hydrocarbons may be prepared by distilling salts of acids with soda-lime or barium hydroxide, or in some cases, with sodium methylate (Mai: Ber., 22, 2133.)

$$RCO_2Na + NaOH = RH + Na_2CO_3.$$

A second method consists in treating halogen derivatives of the hydrocarbons with sodium, usually in ethereal solution, or with zinc alkyl compounds.

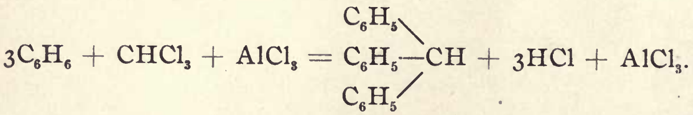
$$RI + R'I + 2Na = R - R' + 2NaI.$$



$$2RI + Zn\begin{matrix}\diagup R' \\ \diagdown R'\end{matrix} = 2R - R' + ZnI_2.$$

These methods are of especial value for the determination of structure.

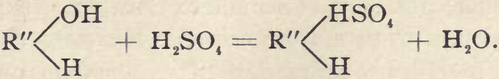
A somewhat related method consists in treating a mixture of an aromatic hydrocarbon and an alkyl chloride, bromide, or iodide with dry aluminium chloride (Friedel and Crafts). This method of synthesis loses very much in value from the fact that side chains of aromatic hydrocarbons may be removed by the action of aluminium chloride, and rearrangements are liable to result. As an illustration of the reaction, the synthesis of triphenyl methane may be given.



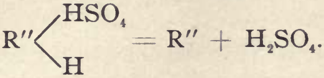
$$3C_6H_6 + CHCl_3 + AlCl_3 = \begin{matrix}C_6H_5\diagdown \\ C_6H_5-CH \\ C_6H_5\diagup\end{matrix} + 3HCl + AlCl_3.$$

The reaction appears to give at first a compound of aluminium chloride with the hydrocarbon, $C_6H_5AlCl_2$, and this compound then reacts with the chloroform forming triphenylmethane and regenerating the aluminium chloride.

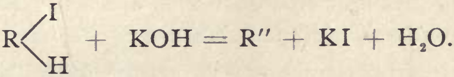
Alcohols are usually converted into unsaturated hydrocarbons when treated with concentrated sulphuric acid, (see 7, p. 44) or zinc chloride, or they may be converted indirectly, by the preparation from them of a halogen alkyl, and treatment of the latter with alcoholic potash.



$$R''\left\langle\begin{matrix}OH\\H\end{matrix}\right. + H_2SO_4 = R''\left\langle\begin{matrix}HSO_4\\H\end{matrix}\right. + H_2O.$$



$$R''\left\langle\begin{matrix}HSO_4\\H\end{matrix}\right. = R'' + H_2SO_4.$$

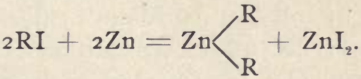


$$R\left\langle\begin{matrix}I\\H\end{matrix}\right. + KOH = R'' + KI + H_2O.$$

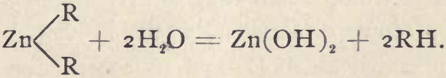
In some cases quinoline may be used with advantage in place of alcoholic potash. (Baeyer: Ber., **25**, 1840, *2122*.)

Monohalogen derivatives of hydrocarbons may be reduced to the hydrocarbon, the reducing agents most commonly used being concentrated hydriodic acid; the copper zinc couple in the presence of alcohol or water (Gladstone and Tribe: Ber., **6**, 202, 454, 1136; J. Chem. Soc., *1884*, 154); zinc in water at 150°-160° (Frankland: Ann., **71**, 203; **74**, 41); and aluminum chloride at 120°-150° (Köhnlein: Ber., **16**, 560; Kluge: Ann., **282**, 214.) The author has found that Köhnlein's method gives a mixture of compounds when applied to isobutyl iodide. The iodides are more suitable than other halogen derivatives for these reactions.

$$RI + HI = RH + I_2.$$



$$2RI + 2Zn = Zn\left\langle\begin{matrix}R\\R\end{matrix}\right. + ZnI_2.$$



$$Zn\left\langle\begin{matrix}R\\R\end{matrix}\right. + 2H_2O = Zn(OH)_2 + 2RH.$$

Compounds having two halogen atoms combined with adjacent carbon atoms, lose both bromine atoms with the formation of an unsaturated hydrocarbon on treatment with sodium, or with zinc dust and acetic acid, or with mercuric iodide, or lead iodide.

Under the influence of condensing agents, such as concentrated sulphuric acid, zinc chloride, and phosphorus pentoxide, or pentasulphide, ketones, aldehydes, and sometimes other compounds, frequently condense to form hydrocarbons. In this way mesitylene is formed from acetone, and cymene from the open chain aldehyde, geranial. (Semmler: Ber., **23**, 2965; **24**, 205.) The formation of cymene from camphor is analogous in some respects, but involves a separation of two carbon atoms instead of a condensation.

A great variety of hydrocarbons, especially methane, olefines, acetylene, and aromatic hydrocarbons, are formed by heating organic compounds to high temperatures.

Aromatic hydrocarbons may be reduced to "alicyclic" compounds by reduction with hydriodic acid at high temperatures, or, sometimes, by means of amyl alcohol and sodium. Zelinsky has shown, however, that hydriodic acid at high temperatures transforms cyclohexane into methyl cyclopentane. (Ber., **30**, 387.)

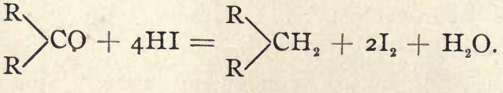
$$C_6H_6 + 6HI = C_5H_9CH_3 + 3I_2.$$

$$C_{10}H_8 + 4H = C_6H_4 \cdot C_4H_8.$$

Naphthalene. Naphthalene tetrahydride

Benzene may be reduced to cyclohexane and many other compounds may take up hydrogen when heated to a moderate temperature with hydrogen in the presence of finely divided nickel. (Sabatier and Senderens, see **11**, p. 50.) Somewhat similar reductions may be effected at ordinary temperatures by hydrogen in the presence of colloidal palladium or finely divided platinum. (Ber., **41**, 1475.) Little has been said about the theory of these reactions but it would seem that the hydrogen gas is separated into hydrogen atoms or ions under the influence of the metal.

Ketones, phenols, alcohols, and in some cases acids, may be reduced to hydrocarbons by heating with concentrated hydriodic acid, or hydriodic acid and phosphorus, usually in sealed tubes.



$$\begin{matrix}R\\R\end{matrix}\!\!>CO + 4HI = \begin{matrix}R\\R\end{matrix}\!\!>CH_2 + 2I_2 + H_2O.$$

Phenols, and sometimes other oxygen compounds, may be reduced to hydrocarbons by distilling over heated zinc dust, usually in a hard glass tube in a combustion furnace.

The carbides of the metals, when treated with water, or with acids, give hydrocarbons which differ with the metal. Calcium carbide gives acetylene, aluminium carbide gives methane, iron carbide chiefly olefines. (Moissan: Compt. rend., **122**, 1462.)

Aromatic amines may be converted into hydrocarbons by treatment with nitrous acid and alcohol (see **100**, p. 212). Sometimes, however, the reaction causes the replacement of the amine group by the ethoxy group, C_2H_5O, instead of hydrogen. (Remsen and his co-workers: Am. Chem. J., **8**, 243; **9**, 387; **11**, 319; **15**, 105; **19**, 163; **20**, 229.)

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5. Preparation of a Hydrocarbon by Distilling the Salt of an Acid with Soda-Lime.—Methane, CH_4.

Literature.—Preparation from sodium acetate and barium oxide, Dumas: Ann., **33**, 81; Ladenburg u. Krügel: Ber., **32**, 1820; From methyl iodide, Gladstone and Tribe: J. Chem. Soc., **43**, 154; From aluminium carbide, Moissan: Bull. soc. chim., **11**, 1012; **15**, 1285; Formation from the elements, Bone and Jerdan: J. Chem. Soc., **71**, 42.

10 grams anhydrous sodium acetate.
10 grams soda-lime.

Grind together and mix intimately in a mortar 10 grams of fused sodium acetate and 10 grams of soda-lime. Put the mixture in a 100 cc. hard glass retort or in a 20 cm. hard glass test-tube. Support the retort or tube with a clamp attached to a retort stand. Connect by means of a delivery tube of india-rubber or glass with bottles and other receptacles filled with water and inverted in a pan or dish. Heat the contents of the retort or tube strongly with a Bunsen burner and collect the gas evolved, allowing the first portions, which contain air, to escape. Perform the following experiments with the gas.

1. Pour the gas upward from one bottle to another. What is the weight of the gram molecular volume of the gas and how does the weight compare with the weight of air?

2. Mix with the amount of air required for complete com-

bustion (assuming that air contains ⅕ of its volume of oxygen) in a 300 cc., wide mouthed, strong bottle and explode the mixture.

3. Fill a test-tube with the gas, introduce 1 cc. of bromine water, stopper the tube and expose to direct sunlight, or for a longer time to diffused daylight.

4. Examine the residue of the materials from which the gas was generated for carbonate.

How many grams of sodium acetate would be required to generate one gram molecular volume of methane? How many liters should 10 grams of the acetate give?

The preparation of benzene, p. 50, is the same in principle as that of methane given here. The method may also be applied to salts of sulphonic acids.

6. Preparation of a Hydrocarbon from a Halogen Compound by Reduction.—Ethane, C_2H_6. Determination of the density.

Literature.—Identity of ethane from electrolysis of acetic acid and from reduction of ethyl iodide, Schorlemmer: Ann., **131**, 76; **132**, 234; Presence in natural gas, L. Smith: Ann. chim. phys., **8**, 566; Preparation from ethyl iodide, Gladstone and Tribe: Ber., **6**, 202; J. Chem. Soc., **45**, 154; Properties Ladenburg and Krügel: Ber., **32**, 1821; Olzewsky: Ber., **27**, 3306; Hainlen: Ann., **282**, 245.

5 grams powdered zinc.
2 per cent. solution of copper sulphate.
10 grams ethyl iodide.
5 cc. alcohol.

Prepare a round bulb, as shown in Fig. 19, sealed to a three-way stop-cock and having a capacity of 100 to 125 cc. Determine the capacity of the bulb by weighing it empty and filled with water at 20° exactly to the stop-cock, using the directions for calculation given on p. 33. Remove the water and dry the bulb thoroughly by warming and exhausting it repeatedly with a good filter-pump. Finally, when cold, exhaust the bulb while connected with a manometer, measuring the pressure of the residual air and the temperature. Place in the balance case and weigh, noting the temperature of the balance case.

Put 5 grams of powdered zinc (30 mesh, such as is used in the Jones reductor) in a 20 cm., heavy walled test-tube, add 5 cc. of a 2 per cent. solution of copper sulphate and shake till the solution becomes colorless. Pour off the solution of zinc sulphate, add more of the copper sulphate and repeat a third and fourth time. Finally wash repeatedly by decantation and once with alcohol. Cover the zinc with 5 cc. of alcohol, close the tube with a stopper having two holes through one of which passes a thistle tube dipping below the surface of the alcohol and through the other a delivery tube connected with two potash bulbs, the first containing alcohol and the second concentrated sulphuric acid. The alcohol is to absorb vapors of ethyl iodide which might escape and the sulphuric acid to remove vapors of alcohol and water. Connect the second bulbs with the exhausted and weighed bulb mentioned above, the stop-cock being placed in such a manner that the first gas will escape through the side tube. To the latter is attached a delivery tube conveying the gas to an inverted bottle for collecting the gas over water. From the generator to the weighed bulb all connections should be made by bringing the glass tubes together within short, tightly fitting pieces of rubber tubing.

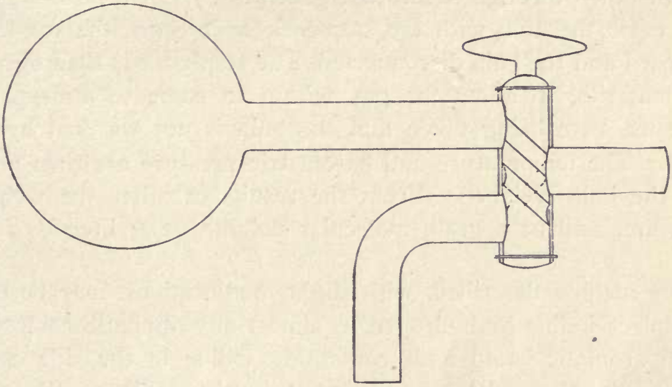


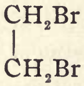
Fig. 19.

When everything is ready, prepare a mixture of 10 grams of ethyl iodide, 5 cc. of alcohol and one or two drops of dilute sulphuric acid. Add this mixture to the generator through the thistle tube, warming very gently at first, if necessary, to start the reaction but cooling later, if the reaction becomes rapid. The mixture must be added carefully, in such a manner that bubbles of air are not carried down the thistle tube. Allow about 300 cc. of gas to collect in the bottle to insure the removal of the air in the apparatus, then turn the stop-cock *very cautiously* so that the gas will enter the exhausted bulb. The column of liquid in the thistle tube must be carefully watched and the gas must not pass into the bulb so fast that air is drawn down through it into the generator. When no more gas will enter the bulb with the stop-cock wide open, the stop-cock is closed and the bulb disconnected. The stop-cock is then opened, momentarily, to allow the gas within to come to atmospheric pressure, care being taken that the bulb is not warmed by the hand. The temperature and barometric pressure are then noted and the bulb weighed. From the results calculate the weights of a liter and of a gram molecular volume (22.4 liters) of the gas.

The method described, with slight modifications, may be used to replace iodine by hydrogen in almost any aliphatic compound or in aromatic compounds containing iodine in the side chain, sometimes, also, when the iodine is in the nucleus. Since alcoholic hydroxyl in alcohols, hydroxy acids and other compounds may usually be replaced by iodine on treatment with concentrated hydriodic acid the method may often be used for the indirect replacement of hydroxyl by hydrogen.

7. Preparation of a Hydrocarbon of the Ethylene Series.—

Ethylene dibromide,



$$\begin{array}{c}CH_2Br\\ |\\ CH_2Br\end{array}$$

(dibrom (1.2) ethane).

Literature.—Balard: Ann chim. phys. [2], 32, 375 (1826); Erlenmeyer and Bunte: Ann., 168, 64; 192, 244; Denzel: *Ibid,* 195, 210; Thorpe: J. Chem. Soc., 37, 177 (1880); Anschütz: Ann., 221, 137; V. Meyer u. Müller: Ber., 24, 4249; Tawildarow: Ann., 176, 12; Use of phosphoric acid, Newth: J. Chem. Soc., 79, 915; Theory for the formation of ether and ethylene, Nef: Ann., 309, 141; 318, 50.

30 cc. alcohol.
50 cc. sulphuric acid (1.84).
50 cc. alcohol.
50 cc. sulphuric acid.
20 cc. (60 grams) bromine.

Put 30 cc. of alcohol in a liter flask. Add 50 cc. concentrated sulphuric acid. Arrange a flask as shown in Fig. 20 with a thistle tube bearing a stopper with a separatory funnel having a short stem. By this arrangement the rate at which the contents of the funnel is dropped into the mixture can be seen and regulated. The lower end of the thistle tube should be drawn out to a diameter of about 2 mm. for about 10 cm. and then bent back twice on itself as shown in Fig. 20. If this is properly done the tube will still pass through the hole of a rubber stopper, and a uniform, slow delivery from the end of the tube can be secured. Connect with a wash-bottle containing caustic soda, and with a second wash-bottle containing concentrated sulphuric acid and having a safety-tube, then with a thick walled tube about 15 mm. in diameter, fitted with tubes like a wash-bottle and containing 20 cc. of bromine covered with a little water. The latter should be placed in cold water and connected with a tube opening just above the surface of a sodium hydroxide solution in a large bottle. Place the generating flask on a thin asbestos paper, and heat till the thermometer (not shown in the figure) in the mixture reaches 170°-175°. It is an advantage to heat momentarily to 185°-190° and then allow the mixture to fall back to the temperature specified. When the evolution of ethylene has well begun, drop in slowly a mixture of 50 cc. of alcohol with 50 cc. of concentrated sulphuric acid, keeping the temperature at about 170°. Continue the passage of the gas till the bromine becomes nearly colorless. The mixture in the generating flask should not carbonize. If it should do so, from too rapid heating, it is usually best to empty the flask and put in a new mixture of alcohol and acid. Transfer the ethylene bromide to a separatory funnel, add some water and agitate gently, separate, add a dilute solution of sodium hydroxide to alkaline reaction, shaking gently with care not to form an emulsion and draw off

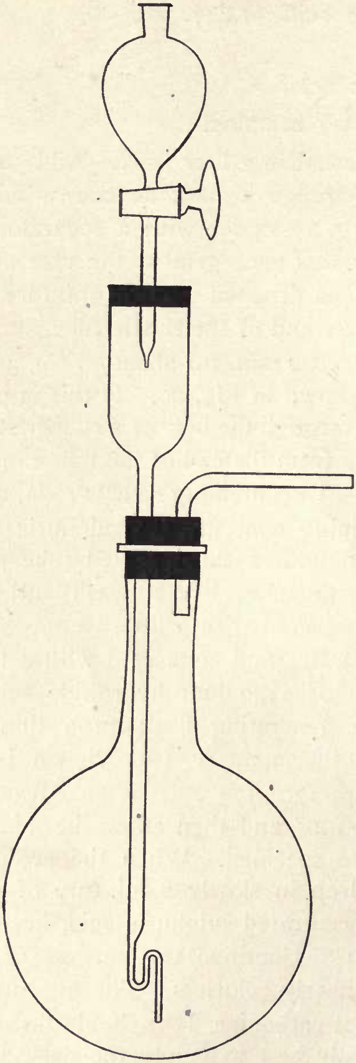


Fig. 20.

into a dry flask. Drops of the ethylene bromide often remain floating on top of the liquid. These can sometimes be caused to settle by gentle agitation but it is usually best to fill the separatory funnel nearly full with water to lessen the area of the upper surface and make it easier to shake down the heavier liquid. Add some fused calcium chloride and allow to stand for sometime to dry the liquid. Filter into a dry distilling bulb, and distil. The yield is nearly equal to the weight of the bromine used.

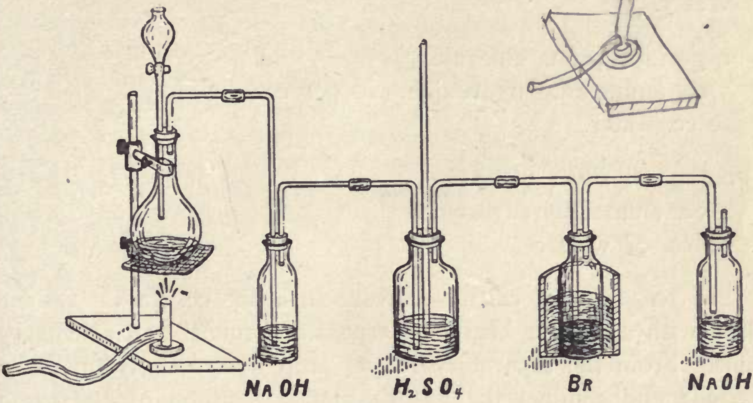


Fig. 21.

Ethylene bromide solidifies at a low temperature and melts at 9.5°. It boils at 130.3°, and has a specific gravity of 2.1785 at 20°. When warmed in alcoholic solution with granulated zinc, ethylene is regenerated. With alcoholic potash vinyl bromide and acetylene are formed. Other compounds having two halogen atoms combined with adjacent carbon atoms react in a similar manner.

8. Preparation of a Hydrocarbon from a Carbide.—Acetylene, $CH \equiv CH$.

Literature.—Preparation of carbides, Moissan: Bull. soc. chim. (3), 11, 1002, 1010; Preparation of hydrocarbons from carbides, Wöhler: Ann., 124, 220; Moissan: Bull. soc. chim., 11, 1012; 15, 1285; Ber., 40, 5120; W. E. Gibbs: Acetylene Gas, its Production and Use; London, 1898; Composition of copper and silver acetylides, Keiser: Am. Chem. J., 14, 285; Söderbaum: Ber., 30, 760; Explosion of acetylene as an endothermic compound, Berthelot, Vielle: Compt. rend., 123, 523; Ann. chim. phys., (7,) 11, 5; Comparative safety of acetylene in acetone, Claude, Hess: Compt. rend., 124, 626; Berthelot, Vieille: Compt. rend., 124, 988, 996, 1000. See also the following preparation.

10 grams of calcium carbide.
Water.

1 gram cuprous chloride.
5 cc. ammonium hydroxide (10 per cent. NH_3.)
20 cc. water.

0.2 gram silver nitrate.
2 cc. ammonium hydroxide.
10 cc. of water.

Put 10 grams of calcium carbide in a 200 cc. flask. Fit the flask with a stopper bearing a separatory funnel and a delivery tube. From the separatory funnel drop water slowly upon the carbide and conduct the gas through a solution of one gram of cuprous chloride dissolved in dilute ammonium hydroxide, also through a solution of 0.2 gram of silver nitrate (2 cc. of a 10 per cent. solution) dissolved in dilute ammonium hydroxide. Filter off the precipitates, transfer them to dry filter-paper and allow to dry in the air. Explode portions of the precipitate by heating over the flame on a piece of tin foil or sheet iron, using very small amounts for the first trials. *Destroy all of the precipitates by explosion or treating with dilute acids before leaving the laboratory.*

If an acetylene burner is available, the illuminating quality of the gas may be tested after all of the air has been expelled from the generator. This may be determined by collecting some of the gas in a test-tube and seeing whether it explodes on the application of a flame.

Acetylene is better generated on a larger scale by dropping the carbide into water and this plan is adopted in the better forms of generators. Why? How many liters of acetylene should 10 grams of calcium carbide yield?

Acetylene tetrabromide may be prepared by passing acetylene into bromine as described on p. 45 for preparing ethylene bromide. It must be distilled under diminished pressure, however.

9. Preparation of a Hydrocarbon by Decomposition of a Halogen Compound with Sodium Ethylate.—Acetylene, $CH \equiv CH$.

Literature.—Formation by incomplete combustion of illuminating gas, Rieth: Z. f. Chemie, 1867, 599; By direct union of carbon and hydrogen, Berthelot: Ann. chim phys., (4), **13**, 143; From vinyl bromide or ethylene bromide and alcoholic potash, Sawitsch: J., 1861, 646; Sabanejew: Ann., **178**, 111; By passing ethylene chloride over heated soda-lime, Wilde: Ber., **7**, 352; By reduction of tetrachlorethane with zinc, Sabanejew: Ann., **216**, 262; By electrolysis of fumaric or maleic acid, Kekulé: Ann., **131**, 85; See also the preceding preparation.

5 grams sodium.
60 cc. absolute alcohol.
10 grams ethylene bromide.

Connect a 200 cc. flask with an upright condenser making sure that the connection is gas tight. A rubber stopper may be used. Put in the flask 5 grams of clean metallic sodium from which the outer crust has been cut with a knife. *The shavings of sodium must be put in the bottle kept for the purpose. It is dangerous to throw them into a slop jar or a sink.* Pour through the condenser, in portions, 60 cc. of absolute alcohol. This may be all added within 5 to 10 minutes but the reaction should not be allowed to become violent. After the alcohol has all been added, boil gently on a wire gauze covered with asbestos till the sodium is all dissolved. Allow to cool, connect the top of the condenser with a small U-tube containing alcohol (to absorb some vinyl bromide, which will escape) and from that to a U-tube or small flask containing a solution of 1 gram of cuprous chloride in 25 cc. of dilute ammonium hydroxide or 0.2 gram silver nitrate in the same solvent. Pour 10 grams of ethylene bromide through the condenser into the cooled solution of sodium ethylate and warm gently to cause a slow evolution of acetylene. Perform the experiments with the copper acetylide and silver acetylide which are described in the preceding preparation.

From the alcohol in the U-tube a small amount of vinyl bromide may be precipitated by adding crushed ice and water. The vinyl bromide boils at 16° and, of course, becomes a gas at ordinary temperatures.

The action of the sodium ethylate in this preparation is similar to the action of alcoholic potash upon almost any aliphatic halogen compound in which the grouping $>CH - CBr\ (Cl, I)<$ occurs, the halogen being removed along with a hydrogen atom which is attached to the carbon atom adjacent to the one bearing the halogen.

Metallic compounds analogous to the copper acetylide (more properly called copper carbide) are formed from all derivatives of acetylene having the grouping $-C \equiv CH$ but not from compounds of the type $R - C \equiv C - R$.

10. Preparation of a Hydrocarbon by Distillation of a Salt of an Acid with Soda-Lime.—Benzene, C_6H_6. (Phen.)

Literature.—Mitscherlich: Ann., 9, 39; Marignac: *Ibid,* 42, 217; Wöhler: *Ibid,* 51, 146; Berthelot: Ann. chim. phys. [4], 9, 469; Hofmann: Ber., 4, 163; Baeyer: *Ibid,* 12. 1311; V. Meyer: *Ibid,* 16, 1465.

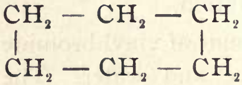
20 grams benzoic acid.
40 grams soda-lime.

Mix 20 grams of benzoic acid with 40 grams of soda-lime by grinding together in a mortar. Put the mixture in a small flask, connect with a condenser, and distil over the free flame. Separate the benzene from the water, dry it with calcium chloride, and distil. If perfectly dry benzene is desired, distil it a second time over metallic sodium. Yield 8 to 9 grams.

Benzene solidifies at a low temperature, and melts at 5.40°. It boils at 80.12°.

This method of preparation is no longer practically used, but it was of very great importance in the early study of the aromatic hydrocarbons, and illustrates a method very general in its application.

11. Reduction of a Hydrocarbon by Hydrogen in the Presence of Finely Divided Nickel. Sabatier's Method.—Cyclohexane,



Literature.—Application of the method to a great variety of substances, Sabatier and Senderens: Ann. chim. phys. (8), 4, 319-488; Compt. rend., **132**, 210, 566; Chem. Centrbl., '01, I, 501, 817; '05, I, 1004, 1317; Reduction of phenol to cyclohexanol, Sabatier and Senderens: Compt. rend., **137**, 1025; Structure of the hydrocarbon formed by reduction of benzene by hydriodic acid, Kijner: J. prakt. Chem. (2), **56**, 364; Description of process, Henle: Anleitung für das organisch präparative Praktikum, p. 79.

Preparation of Finely Divided Nickel

Break some porous porcelain plates into pieces 3 to 5 mm. in diameter and separate them from the dust by means of a sieve. Pour over them in a flat dish a concentrated solution of nickel nitrate and evaporate on the water-bath to dryness, with frequent stirring. When dry, transfer to a nickel crucible and heat over the free flame till no more oxides of nitrogen are evolved. Fill a tube of hard glass, about one meter long and 2 cm. in diameter with the pieces, putting some pieces of broken marble at each end to hold them in place. Draw out one end of the tube and bend it downward or correct with an adapter as shown in Fig. 22.

Place the tube in a combustion furnace inclined at an angle so that the water formed by reduction of the nickel oxide will run away at the lower end, and heat at about 500° (measured with a thermometer filled with nitrogen or carbon dioxide above the mercury) in a rapid current of pure hydrogen for several hours until water no longer condenses in the delivery tube connected with the lower end. The end of the delivery tube should dip under concentrated sulphuric acid to prevent diffusion of air, as only nickel, which has been freshly reduced at not too high a temperature and afterwards portected from the air, is effective. Cool in a slow current of hydrogen.

Arrange the apparatus shown in the figure so that the hydrogen from the Kipp generator passes first through a concentrated solution of potassium permanganate, then through concentrated sulphuric acid, then through a distilling bulb containing 50 grams of benzene. The latter is placed in a beaker of water which can be warmed. Before warming, however, and before connecting the apparatus with the tube containing the reduced nickel the hydrogen is allowed to pass long enough to expel air

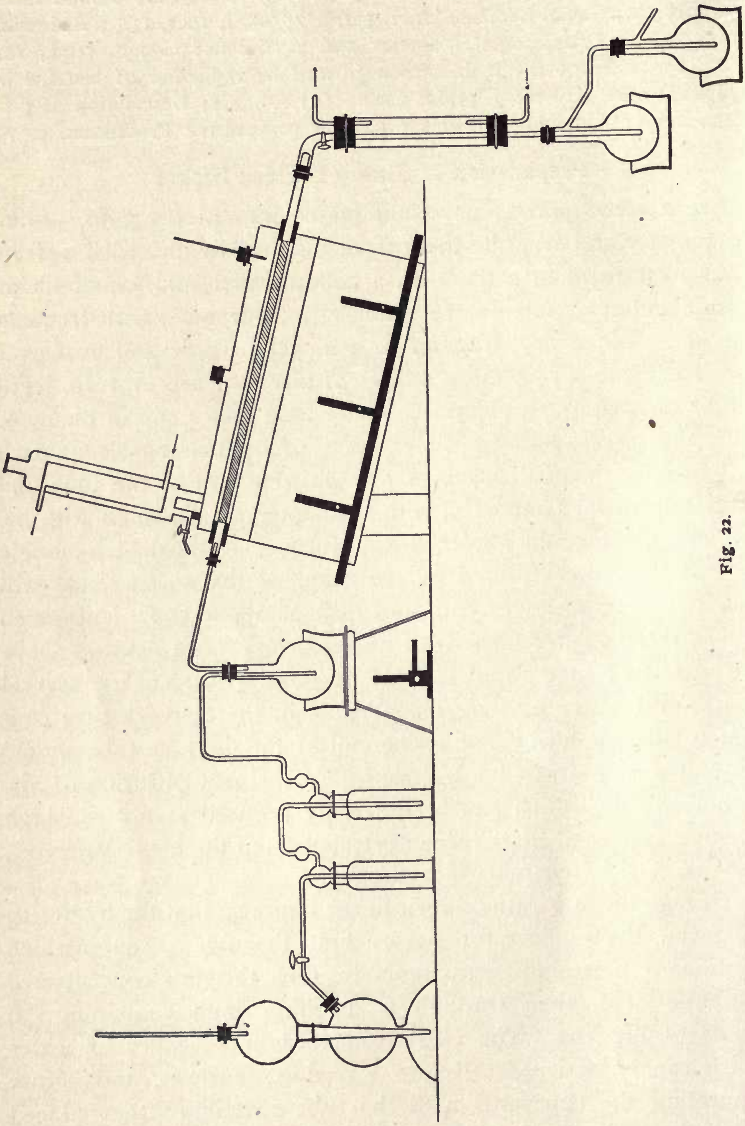


Fig. 22.

from the apparatus. The tube containing the nickel is placed in a Volhard bath (Ann., 284, 235) filled with high boiling gasoline or kerosene which is set to maintain a temperature of 195° by distilling away the low boiling portion till that temperature is reached in the bath. When the air has been expelled, connect the delivery tube of the distilling bulb containing the benzene with the tube containing the nickel and connect the lower end of the latter to a tube reaching just below the neck in a 200 cc. distilling bulb surrounded with ice water. The side tube of this bulb is connected to a tube dipping into 25 cc. of alcohol contained in a second distilling bulb, which is also surrounded with ice water. The alcohol is to retain vapors of cyclohexane which escape condensation in the first bulb.

Maintain the temperature of the bath containing the tube with the nickel at 195°, that of the water in the beaker surrounding the benzene at 35°. At the latter temperature the vapor pressure of benzene is about 145 mm. If the hydrogen is saturated with benzene vapor at that vapor pressure, what per cent. excess of hydrogen will be used? The hydrogen may pass at such a rate that the bubbles may be easily counted. After six or eight hours 30 to 40 grams of cyclohexane should have collected in the bulb surrounded with ice-water. A few grams additional may be obtained by diluting the alcohol contained in the second bulb. The precipitated hydrocarbon is mixed with the rest and the whole shaken, by means of a shaking machine, with an equal volume of fuming sulphuric acid containing 10 to 14 per cent. of sulphur trioxide. This will convert unchanged benzene into benzene sulphonic acid which dissolves easily in water. Pour carefully into 4 or 5 volumes of cold water, cooling after each addition. Separate cyclohexane by means of a separatory funnel, dry with calcium chloride and distil. Yield 70 to 80 per cent. of the weight of benzene used.

Cyclohexane boils at 81° and freezes at a low temperature, melting at 4.7°.

Test the cyclohexane for benzene by warming on the water-bath in a test-tube a few drops with a mixture of 3 cc. of concentrated sulphuric acid and 3 cc. of nitric acid (sp. gr. 1.42). Dilute with water, add a little ether, shake, allow the ether to rise to the top and transfer it to a dry test-tube by means of a pipette with a rubber tube attached. (Fig. 23). Evaporate the ether, by dipping the tube in a water-bath, add 1 cc. of concentrated hydrochloric acid and a piece of tin. After warming a short time, dilute slightly, add a solution of sodium hydroxide in excess, extract with ether as before, and evaporate in a dry test-tube. Test the residue for aniline by dissolving in water and adding a filtered solution of chloride of lime. Try the same test with a drop of pure benzene.

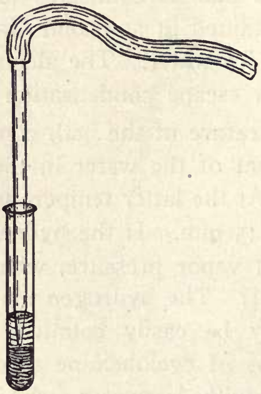
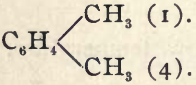


Fig. 23.

The method of reduction discovered by Sabatier may be applied to a great variety of substances, and has made some substances which were formerly very difficult to obtain comparatively easily accessible.

12. Preparation of Hydrocarbons by Means of Halogen Compounds and Sodium. Fittig's Synthesis.—Paraxylene.



$$C_6H_4\begin{cases} CH_3\ (1). \\ CH_3\ (4). \end{cases}$$

(1.4-Dimethylphen.)

Literature.—Synthesis from *p*-bromotoluene, Fittig, Glinzer: Ann., 136, 303; Jannasch: *Ibid,* 171, 79; Ber., 10, 1356; From dibromobenzene: V. Meyer: Ber., 3, 753; Preparation from coal tar through the sulphonic acid; Jacobsen: *Ibid,* 10, 1009, 1356; Crafts: Z. anal. Chem., 32, 243; Compt. rend., 114, 1110.

35 grams parabromotoluene.
35 grams methyl iodide.
12 grams sodium wire.
100 cc. ether.

Press into a 200 cc. flask 12 grams of sodium in the form of wire, add 100 cc. of *dry* ether (see 76, p. 175), place the flask in ice-water, connect with an upright condenser, and add through the latter a mixture of 35 grams of parabromotoluene, and 35 grams of methyl iodide. Allow the mixture to stand over night, or till the reaction appears to be complete. Distil off the ether on the water-bath, and distil the hydrocarbons formed over the free flame. Remove the remainder of the ether from the oil, by allowing it to stand in a crystallizing dish for half an hour *in vacuo* over sulphuric acid. Fraction repeatedly from a small distilling bulb, using test-tubes to collect the distillates, and avoiding loss, as far as possible. Collect as much as possible of the paraxylene, within an interval of 2 to 3 degrees. Cool this portion with ice, or in a freezing mixture, and pour off the part which does not solidify. Yield 5 to 7 grams.

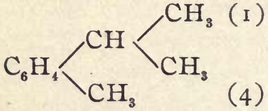
The residue in the flask will contain free sodium and should be treated with alcohol to destroy this and then with water. It must never be allowed to stand or be thrown into a slop jar without this.

Paraxylene melts at 15°, boils at 138°, and has a specific gravity of 0.880 at 0°. It is oxidized by dilute nitric acid to paratoluic acid, and by the chromic acid mixture to terephthalic acid.

This synthesis by means of halogen compounds and sodium, known as the Fittig synthesis, has been very useful in determining the structure of halogen derivatives and of hydrocarbons.

In some cases when the reaction takes place slowly or not at all it may be catalyzed by means of a little *dry* ethyl acetate.

13. Preparation of a Hydrocarbon from Camphor.—Cymene,


$C_6H_4(CH(CH_3)_2)(CH_3)$ (1) (4)

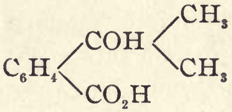
(*p*-Methyl-isopropylphen.)

Literature.—Occurrence, Gerhardt and Cahours: Ann., 38, 71, 101, 345; Preparation from camphor, Gerhardt: *Ibid,* 48, 234; Dumas, Delaland: *Ibid,* 38, 342; by Fittig's synthesis, Sylva: Bull. soc. chim.,43, 321; Jacobsen: Ber., 12, 430; Widman: *Ibid,* 24, 450; From turpentine, Kekulé: *Ibid,* 6, 437; Detection in terpenes, Hartley: J. Chem. Soc., 37, 676; Molecular rearrangements in the formation of cymene, Noyes: J. Am. Chem. Soc., 31, 1372.

30 grams camphor.

30 grams phosphorus pentoxide.

Mix intimately in a flask 30 grams of camphor, and 30 grams of phosphorus pentoxide. Connect with a condenser, and heat in an oil-bath as long as cymene distils. Add to the cymene a little phosphorus pentoxide, and boil a short time with an upright condenser. Pour off, and repeat a second time. Then boil the cymene with some sodium for a short time, using an upright condenser, and finally distil. Yield 15 to 17 grams.

Cymene boils at 175°, and has a specific gravity of 0.8525 at 25°. Potassium permanganate oxidizes it to hydroxypropylbenzoic acid,  $C_6H_4(COH(CH_3)_2)(CO_2H)$; the chromic acid mixture to terephthalic acid; dilute nitric acid to paratoluic acid.

14. Determination of a Hydrocarbon by a Pyrogenic Reaction.—

Diphenyl, $C_6H_5 — C_6H_5$.

Literature.—Preparation by Fittig's syntheses, Fittig: Ann., 121, 363; From benzene at a high temperature, Berthelot: Z. anal. Chem., *1866,* 707; La Coste, Sorger: Ann., 230, 5; From phthalic anhydride and lime, Anschütz, Schultz: Ann., 196, 48; From benzene and tin tetrachloride at a high temperature, Aronheim: Ber., 9, 1898; Smith: *Ibid,* 12, 722; Z. Elektrochemie, 7, 903.

200 cc. benzene.

Fill the central portion of an iron tube, 2 cm. in diameter, and about 50 cm. longer than the combustion furnace, with broken pumice. Connect with one end of the tube, by means of a perforated cork, a tube 15 mm. in diameter, which is drawn out at one end and bent at right angles. Into the wider portion of the tube, which is bent upward, fit a cork bearing a separatory funnel in such a way that the benzene can be seen as it drops from the end of the funnel. Raise this end of the combustion furnace about two inches higher than the other. Connect the other end of the iron tube with a small condenser, by means of a cork and glass tube. Drop benzene from the separatory funnel at the rate of about 15 drops per minute, heating the central portion of the tube to dull redness. When 200 cc. of benzene have been dropped into the tube in this manner, distil the distillate, and return to the separatory funnel the part boiling below 120°. Repeat till a considerable quantity of high boiling products has been obtained. The benzene condenses with evolution of hydrogen.

$$2C_6H_6 = C_6H_5.C_6H_5 + 2H.$$

Fractionate the product and crystallize from alcohol the portion boiling from 235°-300°.

Diphenyl crystallizes in leaflets, which melt at 70°. It boils at 254°, and dissolves in 10 parts of alcohol at 20°.

15. Preparation of a Hydrocarbon by the Reduction of a Ketone with Hydriodic Acid.—Diphenylmethane, $C_6H_5CH_2C_6H_5$.

Literature.—Preparation by reducing benzophenone with hydriodic acid and phosphorus, Graebe: Ber., 7, 1624; With zinc and sulphuric acid, Zincke, Thörner: Ber., 10, 1473; With zinc dust, Staedel: Ann., 194, 307; From benzyl chloride and benzene with zinc dust, Zincke: *Ibid,* 159, 374; By Friedel and Crafts reaction, Friedel, Crafts: Ann. chim. phys. [6], 1, 478; E. and O. Fischer: Ann., 194, 253; By condensing methylal with benzene, Baeyer: Ber., 6, 221.

10 grams benzophenone.
12 grams hydriodic acid (boiling-point 127°).
2.2 grams red phosphorus.

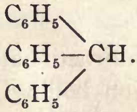
Put in a tube 15 mm. in diameter, and with walls 2 mm. thick, 10 grams of benzophenone, 12 grams of hydriodic acid (boiling-point 127°), and 2.2 grams of red phosphorus. Seal carefully (see p. 20), and heat for 6 hours at 160° in a bomb oven. Open the tube carefully by softening the capillary end in a flame till it blows out. Cut off the end of the tube, add some water and ether to dissolve the hydrocarbon. Separate the ethereal solution, filter it from the red phosphorus, distil off the ether, and distil the diphenylmethane from a small distilling bulb. Yield 8 to 8.5 grams.

Diphenylmethane melts at 26°-27°, and boils at 263°. It is easily soluble in alcohol and ether. It has a specific gravity of 1.0008 at $\frac{26^\circ}{4^\circ}$.

Reduction by means of hydriodic acid has been very often used to replace hydroxyl or oxygen with hydrogen in determining the structure of compounds.

16. Synthesis of a Hydrocarbon by Use of Aluminium Chloride.

(Friedel and Crafts' Reaction.)—Triphenylmethane,



$$(C_6H_5)_3CH$$

Literature.—Preparation from benzylidene chloride and mercury phenyl, Kekulé, Franchimont: Ber., 5, 907; By Friedel and Crafts, reaction, Friedel, Crafts: Ann chim, phys., [6], 1, 489; Compt. rend., 84, 1450; Anschütz: Ann., 235, 208, 337; E. & O. Fischer: *Ibid,* 194, 352; Allen, Köllicker: *Ibid,* 227, 107; Biltz: Ber., 26, 1961; Linebarger: Am. Chem. J., 13, 557; Study of conditions for the reaction, Norris and McLeod: Am. Chem. J., 26, 499; Solubility of triphenylmethane in benzene, Linebarger: Am. Chem. J., 15, 46.

200 grams of benzene.
40 grams chloroform.
20 grams aluminium chloride.

Mix 200 grams of benzene with 40 grams of chloroform, add some fused calcium chloride, and allow the mixture to stand over night. Pour off, or filter, into a *dry* flask, connect the latter with an upright condenser having a calcium chloride tube, which is bent downward, connected with its top. Weigh in a stoppered preparation tube 20 grams of aluminium chloride, best freshly prepared.[1] Add from the tube to the mixture of chloroform and benzene 3 to 4 grams of the aluminium chloride. Shake and warm until the reaction begins; after five to ten minutes add a second portion of the chloride, and add all of it in this manner in about thirty minutes. Boil the mixture gently for an hour, cool, pour carefully into 200 cc. of water, stir, transfer to a separatory funnel, shake, and separate the oil from the water, filter through a filter moistened with benzene to remove water, distil off the benzene, and collect in fractions, below 100°, 100°-200°, 200°-300°. Transfer the residue to a smaller distilling bulb or retort, and distil without a thermometer, or with a thermometer filled with nitrogen under pressure, till the distillate becomes brown and viscous. Crystallize from hot benzene, obtaining in this way the double compound $C_{19}H_{16} + C_6H_6$, which crystallizes in colorless crystals, that melt at 76°. The benzene can be expelled by warming the compound on the water-bath, and the triphenylmethane may be crystallized again from alcohol. Yield 25 to 30 grams, if the aluminium chloride is fresh.

The fraction 200°-300° consists mainly of diphenylmethane (see 51, p. 57).

Triphenylmethane crystallizes in rhombic crystals, which melt at 92°. It boils at 358°-359°. It is easily soluble in ether, chloroform, and hot alcohol, difficultly soluble in cold alcohol.

If a little of the hydrocarbon is dissolved in cold fuming nitric acid, and the solution poured into water, trinitrotriphenylmethane is obtained. This may be reduced to the amino compound by zinc dust and glacial acetic acid. The amine may be precipitated from the filtered and diluted solution by ammonia. If the amine is heated carefully on platinum foil, with a drop of concentrated hydrochloric acid, the red color of the chloride of pararosaniline will be noticed.

17. Preparation of a Hydrocarbon by the Removal of a Hal-

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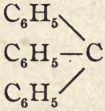
[1] Aluminium chloride may be prepared from aluminium turnings and dry hydrochloric acid gas. (Stockhausen and Gattermann, Ber., 25, 3521; Escales, *Ibid*, 30, 1314.) Gomberg advises the use of chlorine, (Ber., 33, 3146).

ogen atom by Zinc.—Triphenylmethyl and triphenylmethyl peroxide,  $(C_6H_5)_3C$ and $(C_6H_5)_3C—O—O—C(C_6H_5)_3$.

Literature.—Preparation of triphenylmethyl and triphenylmethyl peroxide, Gomberg: J. Am. Chem. Soc., 22, 757; Ber., 33, 3150; 35, 1822; Schmidlin: Ber., 41, 423; Preparation of triphenylchlormethane, Gomberg: J. Am. Chem. Soc., 22, 752; Norris and Sanders: Am. Ch. J., 25, 54; Constitution of triphenylmethyl, Gomberg: Ber., 39 3274; 40, 1847; Gomberg and Cone: Ann., 370, 142; Tschitschibabin: Ber., 37, 4709; 38, 771; 40, 367, 3965; 41, 2421; Baeyer: Ber., 40, 3083; Schmidlin: Ber., 41, 2471; Relation between color and constitution, Curtiss: J. Am. Chem. Soc., 32, 795; Halochromie, Baeyer: Ber., 35, 1189.

2 grams triphenylchlormethane.
3 grams powdered zinc.
10 cc. benzene.

Put in a dry test-tube 2 grams of triphenylchlormethane, 3 grams of powdered zinc and 15 cc. of dry benzene. Seal the tube in the blast and shake at intervals for a day or two. A dark colored oil will collect in the bottom of the tube as the reaction progresses. This oil is a double salt of triphenylchlormethane and zinc chloride. Test one portion of the solution with a solution of iodine in benzene to show the unsaturated character of the triphenylmethyl. Shake another portion of the solution with air and note the formation of triphenylmethyl peroxide.

Triphenylmethyl has aroused very great interest and been the occasion of a very large amount of work on the part of chemists, not only because in some of its forms it seems to have a trivalent carbon atom, but also because of the bearing which many of the facts discovered in connection with it have upon the question of the relation between color and chemical constitution.

18. Preparation of a Hydrocarbon by Reduction with Zinc Dust.—Anthracene, $C_{14}H_{10}$.

Literature.—Preparation from coal tar, Dumas, Laurent: Ann., 5, 10; From toluene, benzene and ethylene at a high temperature, Berthelot: Ann., 142, 254; Behr, van Dorp: Ber., 6, 754; By Friedel and Crafts, reaction, Perkin, Hodgkinson: J. Chem. Soc., 37, 726; From *o*-bromobenzylbromide. The paper contains a list of syntheses of anthracene, Jackson: Am. Chem. J., 2, 384; By distilling alizarin with zinc dust, Graebe, Liebermann: Ann. Supl., 7, 297; Baeyer: Ann., 140, 295; Graebe and Liebermann: Ber., 1, 49.

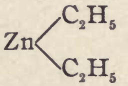
1 gram alizarin.
Zinc dust.

Fill a combustion tube as follows: Put near one end a loose plug of asbestos, then 5 cm. of zinc dust, then a mixture of one gram of alizarin, with 30 grams of zinc dust, then about 30 cm. of a mixture of zinc dust with about ¼ its weight of asbestos, then a plug of asbestos loosely packed. Rap the tube on the table to give a quite free channel above the zinc dust, lay the tube in the combustion furnace, and pass hydrogen from the end first filled till the air is expelled. Heat the mixture of asbestos and zinc to bright redness, slowly, beginning at the rear end, continuing a slow current of hydrogen. Crystallize the anthracene, which sublimes to the front, cooler part of the tube, from benzene or toluene, and determine its melting-point. Also oxidize a part of it with chromic anhydride in glacial acetic acid, and determine the melting-point of the anthraquinone (see 42, p. 103).

Anthracene melts at 216° and boils at 351°.

This method of preparing anthracene is of great historical significance, as it led Graebe and Liebermann to the discovery of the character of alizarin, and so, indirectly, led to its synthetical preparation.

19. Zinc Ethyl,



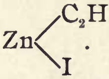
$$\mathrm{Zn}\begin{matrix}\diagup C_2H_5\\ \diagdown C_2H_5\end{matrix}.$$

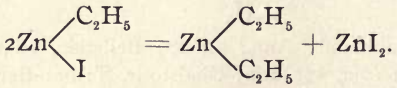
Literature.—Frankland: Ann., 95, 28; Beilstein, Rieth: *Ibid,* 123, 245; 126, 248; Rathke: *Ibid,* 152, 220; Gladstone, Tribe: Ber., 6, 200; J. Chem. Soc., 35, 569; Kaulfuss: Ber., 20, 3104; Haase: *Ibid,* 26, 1053; Arthur Lachman: Am. Chem. J., 19, 410.

18 grams powdered zinc.
2 grams reduced copper.
20 grams ethyl iodide.

Put in a 50 cc. round-bottomed flask 18 grams of powdered zinc,[1] and 2 grams of copper powder, obtained by reducing fine copper oxide in hydrogen at a low temperature. Close the flask with a cork having a small glass tube through it. Heat gently over a free flame, turning all the time till the mass becomes gray and loses its luster, but not till there is any sign of fusion. Seal the glass tube, and allow to cool.

Bend a glass tube, of such size and length as to replace the inner tube of a small Liebig condenser, at an angle of 135° near the end. Insert the tube in the mantle of the condenser, clamp the latter at an angle of 45° with the horizontal, and connect the flask containing the zinc-copper couple to the lower end of the bent tube, with a tightly fitting cork. Pour in through the condenser 20 grams of ethyl iodide. Place a test-tube, large enough to allow a small glass tube to pass into it beside the condenser tube, over the upper end of the condenser, nearly closing the mouth of the test-tube with a cork ring or with paper. Pass into the test-tube a slow current of carbon dioxide, and heat the flask containing the ethyl iodide and zinc-copper couple on the water-bath as long as ethyl iodide continues to distil and run back, usually only a short time. Then turn the condenser in such a way that the main tube of the condenser slants downward, and distil off the zinc ethyl carefully with a free flame, continuing the current of carbon dioxide through the test-tube.

By heating on the water-bath, the ethyl iodide reacts with the zinc, forming ethyl zinc iodide,  $\mathrm{Zn}\left\langle\begin{matrix}C_2H_5\\ I\end{matrix}\right.$. On heating to a higher temperature, zinc ethyl is formed.



$$2\mathrm{Zn}\left\langle\begin{matrix}C_2H_5\\ I\end{matrix}\right. = \mathrm{Zn}\left\langle\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right. + \mathrm{ZnI_2}.$$

On account of its spontaneous inflammability on coming to the air, very great care must be exercised in working with zinc ethyl, and it must be kept in sealed tubes, and in a fire-proof case. Small bulbs can be filled with the substance by preparing them with a small capillary tube on both sides, filling them with carbon dioxide, drawing the zinc ethyl up into the bulb, (if drawn by suction with the mouth a large bulb of some sort should be interposed), and sealing the tube above the bulb with a blowpipe.

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[1] Baker and Adamson's zinc, powdered to pass a 30 mesh sieve, answers well for this purpose. Arthur Lachman (loc. cit.) prepares a zinc-copper couple by mixing zinc dust with one-eighth of its weight of fine copper oxide and reducing in a current of hydrogen at a dull red heat.

Zinc ethyl boils at 118°, and has a specific gravity of 1.182 at 18°. It takes fire spontaneously in the air, or in chlorine, and decomposes violently with water, giving zinc hydroxide and ethane.

Zinc ethyl is introduced here because it has frequently been used for the preparation of hydrocarbons. It was formerly used for a variety of syntheses but nearly everything which has been accomplished by its use is now more conveniently effected by other means. The Barbier-Grignard reaction (p. 65) especially, has replaced it for many purposes.

Chapter IV

ALCOHOLS AND PHENOLS

Alcohols are prepared from the halogen derivatives of hydrocarbons, by treatment with water, potassium carbonate and water, silver oxide and water, or potassium or silver acetate, followed by saponification of the acetic ester of the alcohol, which is formed. The iodides react more readily than other halogen derivatives, but bromides are often used.

$2RI + K_2CO_3 + H_2O = 2ROH + 2KI + CO_2.$
$RI + AgC_2H_3O_2 = R—O—C_2H_3O + AgI.$
$RO — C_2H_3O + KOH = R — OH + KC_2H_3O_2.$

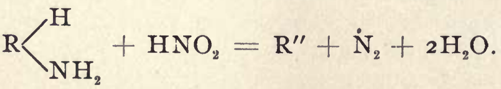
From unsaturated hydrocarbons alcohols can be obtained by dissolving them in concentrated sulphuric acid, diluting, and distilling. The method gives secondary and tertiary alcohols in cases where their formation is possible.

$$C_nH_{2n} + H_2SO_4 = C_nH_{2n+2}HSO_4$$
$$C_nH_{2n+1}HSO_4 + H_2O = C_nH_{2n+1}OH + H_2SO_4.$$

Aldehydes may be reduced to primary alcohols, and ketones to secondary alcohols. The reducing agents most often used are sodium amalgam in aqueous solutions, sodium in alcoholic or moist ethereal solutions, or zinc dust and glacial acetic acid. The last method gives an acetate, which requires saponification.

Amines may be converted into alcohols by the action of nitrous acid in aqueous solutions. In the aromatic series a diazo compound is first formed. In the aliphatic series, and especially in cyclic compounds, unsaturated hydrocarbons are also formed, and interfere seriously with the yield.

$$RNH_2 + HNO_2 = ROH + N_2 + H_2.$$

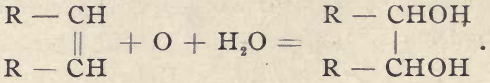


$$R\begin{matrix} H \\ NH_2 \end{matrix} + HNO_2 = R'' + N_2 + 2H_2O.$$

In the aromatic series sulphonic acids, and in many cases halogen derivatives, may be converted into phenols by fusion with potassium hydroxide. The reaction is accompanied, in some cases, by a rearrangement, which interferes with its reliability for the determination of structure.

$$RSO_2OH + 2KOH = ROH + K_2SO_3 + H_2O.$$

Glycols, that is, alcohols having two hydroxyl groups combined with adjacent carbon atoms, may be prepared, in some cases, by oxidizing olefines with a cold solution of potassium permanganate.



$$\begin{array}{l} R - CH \\ \quad\ \ \| \\ R - CH \end{array} + O + H_2O = \begin{array}{l} R - CHOH \\ \qquad\ | \\ R - CHOH \end{array}.$$

This reaction is of greater importance for the preparation of dihydroxy acids than for the preparation of glycols, however. (See Fittig: Ber., **27**, 2670.)

Many aromatic aldehydes, on treatment with potassium hydroxide and water, are converted into a mixture of the potassium salt of the corresponding acid, and the corresponding alcohol.

$$2RCHO + KOH = RCH_2OH + RCO_2K.$$

Barbier[1] and Grignard discovered in 1899-1900 that the organo-magnesium halides of the type R—Mg—Br(I) formed by the action of halogen compounds on magnesium in *dry* ether may be used for a great variety of syntheses. Contrary to its conduct in most other cases the halogen of aromatic as well as of aliphatic compounds may be replaced by reactions carried out at or below the boiling-point of ether by this method and it has practically replaced all reactions for which zinc alkyl compounds were formerly used. The most important applications of the Barbier-Grignard syntheses are the following:

1. Preparation of hydrocarbons, Grignard: Compt. rend., **130**, 1322.

$$R—MgBr + HOH = RH + Mg(OH)Br.$$

$$R—MgBr + R'OH = RH + R'.OMgBr.$$

The second reaction may sometimes be used for the detection and even for the determination of hydroxyl in organic compounds by measuring the amount of methane liberated when methyl magnesium iodide acts upon the compound. Tschugaeff: Ber., 35, 3912; Zerewitinoff: Ber., 40, 2023.

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[1] The reaction has been generally know as the Grignard reaction but it seems to have been first used by Barbier (Comp. rend., 128, 110, (1899)), and Grignard undertook the study of the reaction at the suggestion of Barbier.

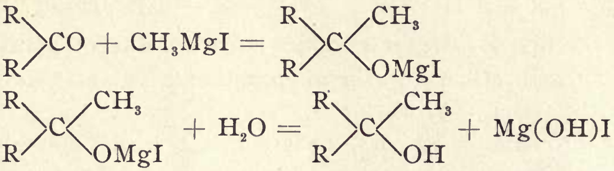
2. Preparation of alcohols.

a. By the successive action of oxygen and water on the organomagnesium halide. Thus pinene chlorhydrate gives borneol:

$C_{10}H_{17}MgCl + O = C_{10}H_{17}OMgCl.$

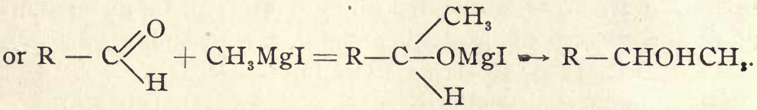
$C_{10}H_{17}OMgCl + H_2O = C_{10}H_{17}OH + Mg(OH)Cl.$

b. By the action of the organomagnesium halide on a ketone or an aldehyde,



$$\begin{matrix}R\\R\end{matrix}\!>\!CO + CH_3MgI = \begin{matrix}R\\R\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\OMgI\end{matrix}$$

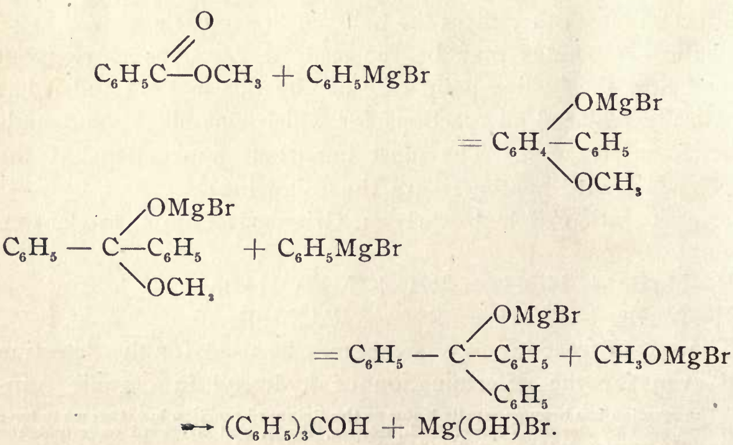
$$\begin{matrix}R\\R\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\OMgI\end{matrix} + H_2O = \begin{matrix}R\\R\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\OH\end{matrix} + Mg(OH)I$$



$$\text{or } R-C\!\begin{matrix}{}^{\nearrow O}\\{}_{\searrow H}\end{matrix} + CH_3MgI = R-\overset{CH_3}{\underset{H}{C}}-OMgI \rightarrow R-CHOHCH_3.$$

Ketones give tertiary alcohols, aldehydes give secondary.

c. By the action of the organomagnesium halide on an ester, giving a tertiary alcohol.

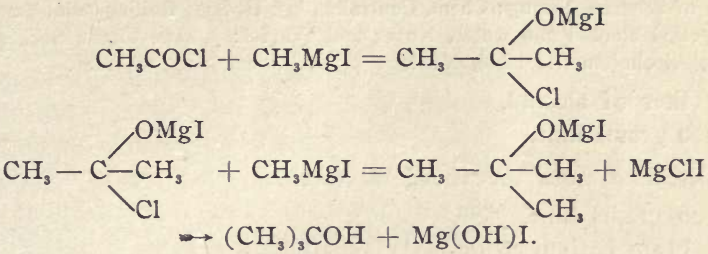


$$C_6H_5\overset{O}{\overset{\|}{C}}-OCH_3 + C_6H_5MgBr = C_6H_4-\overset{OMgBr}{\underset{OCH_3}{C}}-C_6H_5$$

$$C_6H_5-\overset{OMgBr}{\underset{OCH_3}{C}}-C_6H_5 + C_6H_5MgBr = C_6H_5-\overset{OMgBr}{\underset{C_6H_5}{C}}-C_6H_5 + CH_3OMgBr$$

$$\rightarrow (C_6H_5)_3COH + Mg(OH)Br.$$

d. From acid chlorides,



$$CH_3COCl + CH_3MgI = CH_3 - \overset{OMgI}{\underset{Cl}{C}} - CH_3$$

$$CH_3 - \overset{OMgI}{\underset{Cl}{C}} - CH_3 + CH_3MgI = CH_3 - \overset{OMgI}{\underset{CH_3}{C}} - CH_3 + MgClI$$

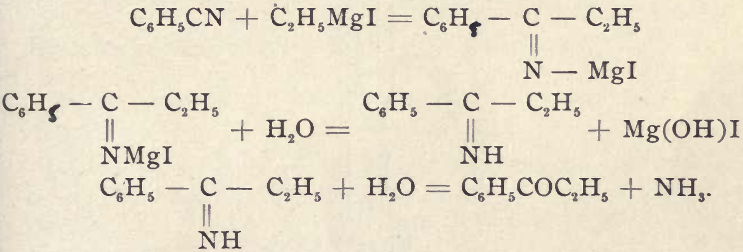
$$\rightarrow (CH_3)_3COH + Mg(OH)I.$$

3. Preparation of aldehydes from orthoformic ester. Grignard: Compt. rend., **138**, 92; Gattermann and Maffezzoli: Ber., **36**, 4152.

$$HC(OC_2H_5)_3 + C_6H_5MgBr = C_6H_5CH(OC_2H_5)_2 + C_2H_5OMgBr.$$

$$C_6H_5 - CH(OC_2H_5)_2 + HCl + H_2O = C_6H_5CHO + HCl + 2C_2H_5OH.$$

4. Preparation of ketones from a nitrile and an organomagnesium halide. Blaise: Comp. rend., 132, 38.



$$C_6H_5CN + C_2H_5MgI = C_6H_5 - \underset{\underset{N - MgI}{\|}}{C} - C_2H_5$$

$$C_6H_5 - \underset{\underset{NMgI}{\|}}{C} - C_2H_5 + H_2O = C_6H_5 - \underset{\underset{NH}{\|}}{C} - C_2H_5 + Mg(OH)I$$

$$C_6H_5 - \underset{\underset{NH}{\|}}{C} - C_2H_5 + H_2O = C_6H_5COC_2H_5 + NH_3.$$

The literature of the Barbier-Grignard synthesis is very voluminous. The following authors have prepared good summaries; Tscheiinzeff: Ber., 37, 2081; C. E. Waters: Am. Chem. J., 33, 304; Alex, McKenzie. British Assoc. Report, Section B, Leicester, 1907. See also Chem. Centralbl., 1901, II, 62, and Schmidt, Ahren's Sammlung, 10, 67, and 13, 357, complete bibliography.

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20. Preparation of Absolute Ethyl Alcohol, CH_3CH_2OH.

Literature.—Use of lime, Soubeiran: Ann., 30, 356; Erlenmeyer: Ann., **160**, 249; Warren: J. Am. Chem. Soc., 32, 698; Use of barium oxide to indicate the end, Berthelot: Jahresb., 1862, 392; Use of calcium carbide, Yvon: Compt. rend., **125**, 1181; Ostermayer: Chem. Centralbl., '98, I, 658; Use of benzene, Young: Chem. Centralbl., '03, II, 869; Boiling-point curve for ethyl alcohol and water, Noyes and Warfel: J. Am. Chem. Soc., **23**, 463; Alcoholometric table, Morley: J. Am. Chem. Soc., **26**, 1186.

1 liter of alcohol.
300 grams lime.

Distillate from the above mixture.
200 grams lime.
1 gram barium oxide.

Put 300 grams of good lime in a 1,500 cc. flask. Add 1 liter of ordinary alcohol and allow to stand over night. Place the flask on a water-bath, connect with an upright condenser (Fig. 24) and boil gently for two hours. Then connect with the condenser by means of a bent tube and distil away the alcohol, collecting it in a dry flask. Add to the distillate 200 grams of lime and about one gram of barium oxide. Allow to stand over night and then connect with the upright condenser as be-

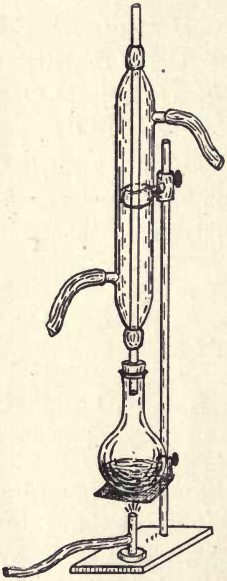


Fig. 24.

fore and boil for two hours or until the barium oxide dissolves imparting a yellow color to the alcohol. Distil away the alcohol as before but collect in a distilling bulb connected to the lower end of the condenser with a tightly fitting cork and having a calcium chloride tube connected to its side tube to prevent moist air from entering the bulb. Determine the specific gravity and strength of the alcohol (p. 32).

The boiling-point of absolute alcohol is 78.3° (Ramsey and Young: J. Chem. Soc., **47**, 640). Its specific gravity at 20° is 0.78932. It will not cause anhydrous copper sulphate to turn blue even on long standing with it and it will not evolve acetylene with calcium carbide.

If turnings of metallic calcium are available, the last portions of water may be removed more rapidly by warming the alcohol with these.

Prepare some sodium ethylate by dissolving a piece of sodium the size of a pea in 1 cc. of absolute alcohol in a test-tube. If the alcohol is absolute and the solution sufficiently concentrated, it will solidify on cooling. Notice also that such a solution darkens rapidly on exposure to the air while a solution of sodium hydroxide in pure alcohol darkens slowly, if at all.

21. Preparation of an Unsaturated Alcohol.—Allyl alcohol, $CH_2 = CH — CH_2OH$. (1.3-propenol).

Literature.—Berthelot and de Lucca: Ann., **100**, 359; Cahours and Hofmann: *Ibid*, **102**, 285; Aronheim: Ber., **7**, 1381; Tollens, Henninger: Ann., **156**, 134, 142; Tollens: *Ibid*, **167**, 222; Romburgh: Jahresb., *1881*, 508; Bigot: Ann. chim. phys., [6], **23**, 464.

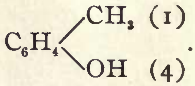
200 grams glycerol.
50 grams crystallized oxalic acid.
0.25 gram ammonium chloride.

In a 300 cc. distilling bulb put 200 grams of glycerol, 50 grams of crystallized oxalic acid, and ¼ gram of ammonium chloride, the last being added to decompose any alkali salts present, which would interfere with the reaction. Insert a thermometer, immersed in the liquid, and connect with a condenser. Heat gently so that the temperature rises slowly. The portion distilling below 195° consists mainly of dilute formic acid (see **45**, p. 115), and may be converted into the lead salt by boiling with lead carbonate. Collect by itself the portion coming over from 195° to 240°. When the latter temperature is reached, cool, add 30 grams of oxalic acid and distil as before.

Unite the distillates (195°-240°) and distil, collecting the portion boiling below 105°. Add dry potassium carbonate till the allyl alcohol separates above, separate and add 10 per cent. of its weight of powdered caustic potash, and allow the mixture to stand for some time, until the odor of acrolein has disappeared, separate and distil, collecting the portion boiling at 90°-96°. In order to remove the last traces of water, it is necessary to distil again, after standing for some time with lime or barium oxide. Yield 12 to 15 grams.

Allyl alcohol boils at 96.6°, and has a specific gravity of 0.8573, at 15°. When dilute allyl alcohol is treated with bromine dissolved in a solution of potassium bromide, the dibromide, $CH_2BrCHBrCH_2OH$, is formed, and the reaction may be used for quantitative determinations.

22. Preparation of a Phenol by the Decomposition of an Amine through the Diazonium Compound.—Paracresol,



$C_6H_4\begin{cases} CH_3 & (1) \\ OH & (4) \end{cases}$.

(*p*-Methyl phenol.)

Literature.—Stüdeler: Ann., 77, 17; Salkowski: Ber., 12, 1440; Griess: Jahresb., *1866*, 458; Körner: Ztschr. Chem., *1868*, 326; Wurtz: Ann., 144, 129; Fittig and Kiesow: 156, 258; Oudemans: *Ibid*, 170, 259; Southworth: *Ibid*, 168, 271; Pinette: *Ibid*, 243, 43.

20 grams paratoluidine.
600 cc. water.
20 cc. concentrated sulphuric acid.

15 grams sodium nitrite.
75 cc. water.
2 grams urea.

30 cc. sodium hydroxide (3 cc. = 1 gram).
10 cc. concentrated sulphuric acid.
30 cc. water.

In a one liter flask put 20 grams of paratoluidine, 600 cc. of water, and 20 cc. of concentrated sulphuric acid. Heat till dissolved. Cool to 20° or below, and add slowly, with shaking, a solution of 15 grams of sodium nitrite, in 75 cc. of water, keeping the temperature below 20°. Allow to stand for a short time, add 2 grams of urea, connect with a condenser, and distil over the paracresol with water vapor. For this purpose the flask is fitted as shown in Fig. 25 with a stopper bearing two glass tubes. One of these should reach nearly to the bottom of the flask or distilling bulb and should be bent to one side in such a manner that the escaping steam will give a rotary motion to the liquid. The flask should be inclined so that the steam will throw the liquid upward toward the side of the flask and not into its neck. The second tube connects with the condenser. The steam is best generated in a two quart can of tin, copper or galvanized iron. The stopper of the can bears two tubes, one about a meter long reaching nearly to the bottom of the can, the other a short bent tube to carry away the steam. The latter is connected with the longer tube in the flask by means of a rubber tube.[1] Continue the distillation till the distillate gives no turbidity with bromine water. Add to the distillate 30 cc. of a strong solution of caustic soda and a little bone-black, and

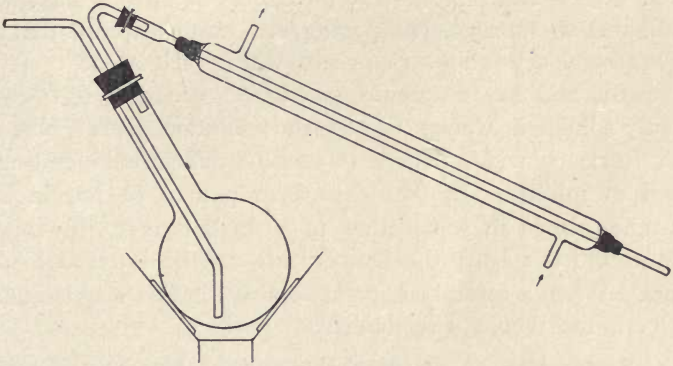


Fig. 25.

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[1] For a simple apparatus for steam distillation, using a reversed condenser, see Mathews, J. Chem. Soc., 71, 318.

concentrate rapidly to about 75 cc. by boiling in a large lip beaker, covered with a watch-glass, to prevent oxidation. Filter into a beaker containing 10 cc. of concentrated sulphuric acid diluted with 30 cc. of water. Cool, and extract the cresol with ether, extracting three or four times. Dry the solution for a few minutes with calcium chloride, pour off, distil the ether from a water-bath, dry the residue *in vacuo* over sulphuric acid, and distil. Yield 15 to 16 grams.

The urea is added to destroy the excess of nitrous acid, which, if allowed to remain, would interfere seriously with the yield.

Paracresol crystallizes in prisms which melt at 36°. It boils at 201.8°, and has a specific gravity of 0.9962 at 65.6°. It is slightly soluble in water. Its aqueous solution gives a blue color with ferric chloride. There is usually difficulty in getting the cresol to solidify. In that case a drop may be put in a dry test-tube, placed in some ether in a small beaker. By blowing air through the ether the temperature can be lowered to 0° or below. When a crystal of cresol obtained in this way is added to the rest, the whole will solidify.

23. Preparation of an Alcohol of the Aromatic Series by Treatment of an Aldehyde with Caustic Potash.

—Benzyl alcohol, $C_6H_5CH_2OH$ (phenmethylol).

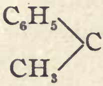
Literature.—Kraut: Ann., 152, 129; Busse: Ber., 9, 830; Cannizzaro: Ann., 88, 129; 96, 246; Herrmann: *Ibid,* 132, 76; Lauth, Grimaux: *Ibid,* 143, 81; Niederest: *Ibid,* 196, 353; Kachler: Ber., 2, 514; R. Meyer: *Ibid,* 14, 2394; Graebe: *Ibid,* 8, 1055.

30 grams benzaldehyde.
27 grams potassium hydroxide.
25 cc. water.

Dissolve 27 grams of caustic potash in 25 cc. of water, add the solution to 30 grams of benzaldehyde, and shake till an emulsion is formed. Allow the mixture to stand for 24 hours. Add enough water to dissolve the potassium benzoate, and extract with ether. Distil off the ether, dry under diminished pressure with a capillary (see 75, p. 171 and 138), and distil with an air condensing tube. From the alkaline solution the benzoic acid may be precipitated and purified by recrystallizing from hot water. Yield 14 to 15 grams, if the benzaldehyde used is free from benzoic acid.

Benzyl alcohol boils at 204.7°, and has a specific gravity of 1.0507 at 15.4°. It dissolves in 25 parts of water at 17°. It combines with calcium chloride, and cannot be dried by that agent.

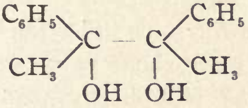
24. Preparation of an Alcohol by the Reduction of a Ketone.—

Phenyl methyl carbinol,  phenethylol (1).

Literature.—Radziszewski: Ber., 7, 141; Berthelot: Ztschr. Chem., *1868*, 589; Emmerling, Engler: Ber., 4, 147; 6, 1006.

10 grams acetophenone.
100 cc. ether.
30 cc. water.
8-10 grams sodium.

Put in a 200 cc. flask 10 grams of acetophenone,[1] 30 cc. of water, and 100 cc. of ether. Add sodium in small pieces, shaking gently, and cooling the flask with water, till the ethereal solution no longer gives a turbidity when a drop of it is put in a test-tube with a dilute solution of phenyl hydrazine acetate (see p. 89). 8-10 grams of sodium will usually be required. Toward the close more water may be added, if the solution of the sodium takes place too slowly. Separate the ethereal solution, distil off the ether, dry the residue *in vacuo* over sulphuric acid, or by heating on a water-bath under diminished pressure with a capillary (pp. 171 and 138), and distil. Yield 6 to 7 grams. The yield is diminished by the formation of the pinacone.



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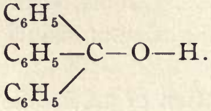
[1] This may be prepared exactly as directed for benzophenone (p. 101), using 12 grams of acetyl chloride in place of 20 grams of benzoyl chloride. The yield is about 12 grams of acetophenone. It melts at 20.5° and boils at 202°. Acetophenone may also be prepared by bringing together equivalent amounts of benzoic acid and acetic acid with some water, and a little more than the equivalent amount of calcium carbonate, evaporating to dryness and distilling the residue from a retort or flask.

Phenyl-methyl-carbinol boils at 202°-204°, and has a specific gravity of 1.013.

25. Preparation of a Tertiary Alcohol from an Ester by Means of a Magnesium Organic Compound.—Barbier and Grignard's Synthesis, Triphenyl Carbinol.



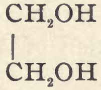
Literature.—Preparation from triphenyl methane, Hemilian: Ber., 7, 1206; By Barbier ad Grignard's reaction, Ullmann and Münzhuber: Ber., 36, 404; Grignard: Compt. rend., 130, 1322 (alcohols, hydrocarbons); 132, 853 (Organometallic compounds of Mg.); 133, 1182 (Compounds from bromobenzene and esters of ketones); Centralblatt., 1901, II, 622 (acids from alkyl halides and carbon dioxide, secondary alcohols from aldehydes and tertiary alcohols from ketones and from esters); W. Tschelinzeff: Ber., 37, 2081 (List of reactions); C. E. Waters: Am. Chem. J., 33, 304 (Report and bibliography); Alex McKenzie: British Association Reports, Section B. Leicester, 1907.

4.8 grams magnesium ribbon.
100 cc. dry ether.
40 grams bromobenzene.
30 grams ethyl benzoate.
10 cc. sulphuric acid (1:1).

Take 200 cc. of ether which has been dried by distillation over calcium chloride (p. 175) add 15 grams of phosphorus pentoxide and allow to stand over night. Pour into a distilling bulb containing 10 grams of phosphorus pentoxide, boil with an upright condenser and with the side tube closed, for an hour, then distil, collecting in a dry distilling bulb attached tightly to the lower end of the condenser with a cork and having the side neck directed upward and protected from moisture by means of a calcium chloride tube. Discard, or use for some other purpose the first 10 cc. of ether collected, also leave about 15 cc. of ether undistilled in the flask containing the phosphorus pentoxide.

Put in a 200 cc. flask 4.8 grams of clean magnesium ribbon, add a crystal of iodine and 100 cc. of the dry ether, then 40 grams of bromobenzene. Cool with ice-water, if the reaction is violent or, if the reaction does not begin, warm gently on a water-bath connecting the flask, in either case, with an upright condenser, the upper end of which is protected by a soda-lime tube. If magnesium phenyl bromide separates, add more dry ether in sufficient amount to keep it in solution. When the magnesium has been dissolved, cool and add through the condenser, dropping it slowly from a dropping funnel, 30 grams of ethyl benzoate which has been allowed to stand for a day with anhydrous sodium sulphate and distilled. The ethyl benzoate is weighed, of course, after distillation.

Boil the mixture gently for an hour with an upright condenser, cool and pour the mixture into a beaker containing broken ice and 10 cc. of sulphuric acid (1:1 by volume). Separate the ethereal layer shake it three times vigorously with 20 cc. of dilute sulphuric acid (5 per cent). Distil off the ether from a distilling bulb and distil the residue with steam (p. 71) as long as bromobenzene or ethyl benzoate passes over. Cool, filter off the triphenyl carbinol, and wash and recrystallize from alcohol. Yield 15 to 18 grams. Triphenyl carbinol melts at 162°. It dissolves in concentrated sulphuric acid with an intense yellow color.

26. Preparation of a Diacid Alcohol from a Halogen Derivative of a Hydrocarbon.—Ethylene glycol,  $\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$ (Ethanediol).

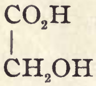
Literature.—Wurtz: Compt. rend., 43, 199, (*1856*) Jeltekow: Ber., 6, 558; Niederest: Ann., 186, 393; 196, 354; Erlenmeyer: *Ibid,* 192, 244; Stempnewsky: *Ibid,* 192, 241; Wagner: Ber., 21, 1234, 3346; Haworth and W. H. Perkin, Jr.: J. Chem. Soc., 69, 175.

18.8 grams ethylene bromide (three times repeated).
13.8 grams potassium carbonate (three times repeated).
100 cc. water.

Put in a 200 cc. flask 18.8 grams of ethylene bromide, 13.8 grams of dry potassium carbonate, and 100 cc. of water. Connect with a reversed condenser, and boil gently till the ethylene bromide disappears, usually eight to ten hours. Add the same amounts of ethylene bromide and potassium carbonate, and boil as before. Repeat a third time. The addition of a few small pieces of wood will help to prevent bumping. Some vinyl bromide, $CH_2 = CHBr$, escapes during the boiling, and can, if desired, be converted into tribromomethane, by leading through a bottle containing bromine. If large amounts of glycol are desired, the addition of ethylene bromide and potassium carbonate may be repeated six times instead of three, but in that case it is necessary to filter off the potassium bromide, which separates, on cooling the solution after each boiling.

Concentrate the solution *in vacuo* over sulphuric acid, pour off from the potassium bromide which separates, wash the latter with a little absolute alcohol, and submit the glycol to fractional distillation. Or the aqueous solution may be distilled at once, best under diminished pressure, and the distillate used in a new preparation, since the glycol is quite volatile with water vapor.

Ethylene glycol is a colorless liquid, with a sweet taste. It boils at 197°, and solidifies in a freezing mixture. It is miscible in all proportions with water and alcohol, but not with ether. Platinum black oxidizes it to glycollic acid,



$$\begin{array}{l} CO_2H \\ | \\ CH_2OH \end{array}$$

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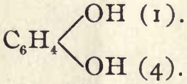
27. Preparation of a Dihydroxy Compound from an Amine through the Quinone.—Hydroquinone,



$$C_6H_4\begin{cases} OH\ (1). \\ OH\ (4). \end{cases}$$

(1.4-Phendiol).

Literature.—Workresenski: Ann., 27, 268; Wöhler: *Ibid,* 45, 354; Nietski: *Ibid,* 215, 127; Ber., 19, 1467; Schniter: *Ibid,* 20, 2283; Wöhler: Ann., 51, 152; Strecker: *Ibid,* 107, 229; Salkowski: Ber., 7, 1010; Hlasiwetz: Ann., 175, 67; Weselski and Schuler: Ber., 9, 1160; Richter: J. prakt. chem., [2], 20, 207, (*1879*); Herrmann: Ann., 211, 336; Ekstrand: Ber., 11, 713; Clarke: Am. Chem. J., 14, 555; Nef: *Ibid,* 12, 483; Seyda: Ber., 16, 687; Theory of the preparation, Willstätter and Dorogi: Ber., 42, 2147.

10 grams aniline.
250 cc. water.
80 grams (44 cc.) concentrated sulphuric acid.
30 grams sodium pyrochromate.
120 cc. water.
Sulphur dioxide.

Put in a beaker 10 grams of aniline, 250 cc. of water, and 80 grams (44 cc.) of concentrated sulphuric acid. Put the beaker in ice-water or a freezing mixture, and cool to 5°. Stir the solution by means of a turbine or hot air motor, and drop in very slowly a solution of 10 grams of sodium pyrochromate in 40 cc. of water. Allow the solution to stand in a cool place over night, and then add, with stirring and cooling, as before, 20 grams of the pyrochromate, dissolved in 80 cc. of water. The temperature should not rise above 10° during the addition of the salt. If the sodium pyrochromate can not be had, very finely powdered potassium pyrochromate may be used instead. After five or six hours, pass into the solution, which now con-

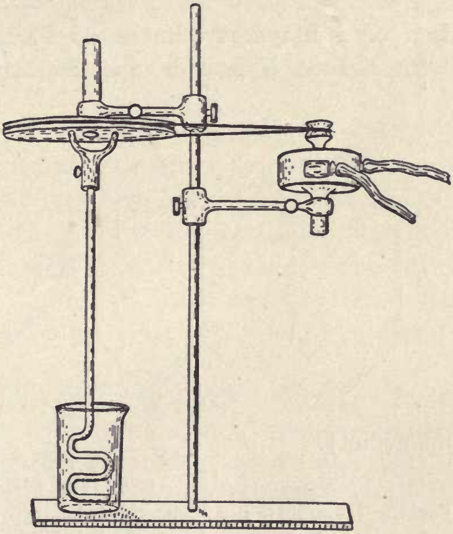


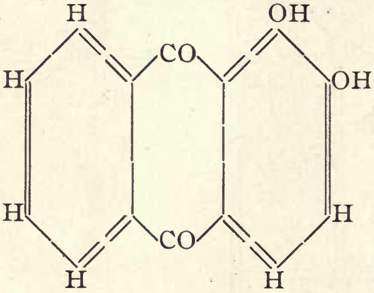
Fig. 26.

tains quinone, $C_6H_4O_2$, a rapid current of sulphur dioxide[1] till the solution smells very strongly of the gas. If the odor of the gas disappears after two hours, pass in more of the gas and allow the mixture to stand again. Extract the solution several times with ether (see 74, p. 167), distil off the ether, and crystallize the hydroquinone from water, using a little bone-black to decolorize it, and a little sulphur dioxide to prevent oxidation. Yield 6 to 8 grams. The yield may be increased by using the bichromate at first to form aniline black and oxidizing the latter with lead peroxide, Willstätter and Dorogi: Ber., 42, 2161.

Hydroquinone crystallizes in colorless prisms, which melt at 169°. It is soluble in 17 parts of water at 15°.

28. Preparation of a Dihydroxyquinone by Fusion of a Sulphonic Acid with Sodium Hydroxide and Potassium Chlorate.

—Alizarin,



(1.2-Anthraquinonediol).

Literature.—Graebe, Liebermann: Ann., 160, 131; Liebermann: Ber., 7, 805; A. G. Perkin, Hummel: J. Chem. Soc., 63, 1167; Liebermann, Graebe: Ann. Supl., 7, 296; Ber., 1, 49, 104, 106; 3, 359; Perkin: J. Chem. Soc., 2, 576, (*1876*); Gerstl: Ber., 9, 281; Liebermann, Lifschütz: Ber., 17, 901; Lagodzinski: Ber., 28, 1422, 1427.

10 grams anthraquinone.
25 cc. fuming sulphuric acid (sp. gr. 1.875 at 25°).
200 cc. water.
50 grams salt.

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[1] This is most easily generated by dropping concentrated sulphuric acid into a 40 per cent. solution of acid sodium sulphite.

10 grams sodium anthraquinone sulphonate.
40 grams sodium hydroxide.
5 grams water.
3 grams potassium chlorate.

Put in a small flask 10 grams of anthraquinone, and 25 cc. of fuming sulphuric acid (containing 10 to 12 per cent. of the anhydride; sp. gr. 1.875 at 25°). Cover with a small watch-glass, and heat to 200°-230° in an oil-bath, raising the temperature to this point slowly, for about two hours, or till a drop of the solution separates little or no anthraquinone on dilution with water. Allow to cool, pour into 200 cc. of water, filter, if necessary, and add 50 grams of salt, stir thoroughly and allow to stand for some time, in cold water, till the sodium anthraquinone sulphonate separates. Filter off, press, and dry on porous porcelain.

In a nickel or iron crucible put 40 grams of sodium hydroxide, and 5 cc. of water, and warm gently till the mass melts, then stir in a mixture of 10 grams of the sodium anthraquinone sulphonate, with 3 grams of potassium chlorate. The latter is for the purpose of oxidizing to alizarin the hydroxyanthraquinone which is formed by fusion with the sodium hydroxide, from the monosulphonate. Heat gently and stir for five to ten minutes, and cool.

The transformation may also be effected with advantage in an autoclave, or in an iron tube (Mannesmann tube), having a cap screwed on the end which is made tight with a lead washer. In that case use 40 cc. of water instead of 5 cc., and heat for 20 hours at 170°.

Dissolve the fused mass in hot water, filter, neutralize the hot solution with hydrochloric acid (150 cc., sp. gr. 1.11), filter off, wash, and dry the precipitated alizarin. The alizarin may be crystallized from alcohol, glacial acetic acid, or nitrobenzene. It may also be obtained in beautiful crystals by sublimation. For this purpose sink a porcelain crucible, about 5 cm. in diameter, in a sand bath to its edge, cover it with a round filter, place on this a funnel of the same size as the crucible, with the stem closed with a rubber cap, or bit of rubber tubing, with a rod in it. Having put the alizarin in the crucible, heat gently till the crystals begin to appear in the funnel. Then remove the flame, or lower it, and allow the whole to stand till the sublimation is complete. If the apparatus shown in Fig. 27 is available, better results may be obtained in the sublimation. The apparatus was designed by Brühl and consists of a hollow plate which can be cooled with a current of water and covered above with a glass dish having a ground edge to fit the plate closely. Yield 2 to 3 grams. By use of an autoclave the yield of crude alizarin is about 7 grams.

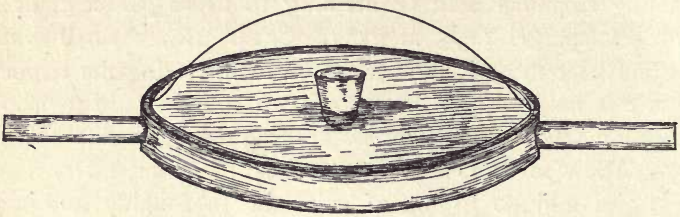

Fig. 27.

Alizarin crystallizes in long, orange-red prisms, which melt at 289°-290°. It boils with some decomposition at 430°, but may be sublimed even at 140°. It is almost insoluble in cold water, easily soluble in alcohol, and ether. It dissolves in alkalies to a purple solution. In dyeing with it, an aluminium mordant gives a red, a ferric salt a violet, and a chromium salt a reddish brown. By distillation with zinc dust, alizarin is reduced to anthracene, the reaction which first led to a knowledge of its composition. (Graebe and Liebermann: Ber., 1, 49).

Chapter V

ETHERS

Methyl ether, ethyl ether and some of their homologues as well as some mixed ethers may be prepared by distilling a mixture of the corresponding alcohols with concentrated sulphuric acid. The reaction involves two steps which proceed side by side.

$$ROH + H_2SO_4 = RHSO_4 + H_2O.$$
$$RHSO_4 + ROH = R{-}O{-}R + H_2SO_4.$$

In the first reaction the alcohol reacts as a base, in the second it reacts as an acid.

Krafft has shown that benzene sulphonic acid may be used to advantage in place of sulphuric acid. Ber., 26, 2830.

Ethers may also be prepared by the action of alkyl halides or of alkyl sulphates upon the sodium derivative of an alcohol.

$$C_2H_5ONa + C_2H_5I = (C_2H_5)_2O + NaI.$$
$$C_6H_5ONa + (CH_3)_2SO_4 = C_2H_5OCH_3 + NaCH_3SO_4.$$
$$C_6H_5ONa + NaCH_3SO_4 = C_6H_5OCH_3 + Na_2SO_4.$$

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29. Preparation of an Ether by Means of Concentrated Sulphuric Acid.—Ethyl ether, $C_2H_5 - O - C_2H_5$.

Literature.—Theory of etherification, Williamson: Papers on etherification; Alembic Club reprint; see also Quart. J. Chem. Soc., 4, 229, (1852); Ann., 77, 37; 81, 73; Nef: Ann., 309, 141; 318, 50; Velocity of the reaction, Conrad and Brückner: Z. physik. Chem., 4, 631; Use of sulphonic acids, Krafft: Ber., 26, 2829; Combination of ether and of ethyl alcohol with magnesium bromide, Menschutkin: Z. anorg. Chem., 49, 34; 52, 9.

100 g. alcohol (125 cc.).
180 g. concentrated sulphuric acid (100 cc.).
100 g. alcohol.

Put 100 grams of alcohol in a 500 cc. flask or distilling bulb, add in portions, with cooling, 180 grams of concentrated sulphuric acid. Fit the mouth of the flask with a cork bearing a thistle tube dipping below the surface of the mixture and carrying a stopper through which passes a separatory funnel with a short stem as shown in Fig. 20, p. 46, also a thermometer dipping into the liquid and a bent tube connecting with a Liebig's condenser. In all cases such connections with the condenser should be made with a tightly fitting *cork* stopper and the stopper in the flask is also best of cork, as ether softens india rubber. Heat the mixture on a wire gauze or asbestos plate till it reaches a temperature of 140°. Then allow the alcohol to drop in slowly and boil gently, maintaining a temperature of 140°-145° by regulating the flow of alcohol and the height of the flame. Allow 100 grams of alcohol to flow into the mixture.

Transfer the distillate to a separatory funnel, add 25 to 50 cc. of water and enough sodium hydroxide so that after vigorous shaking the lower, aqueous layer reacts strongly alkaline. In shaking a mixture of ether and an aqueous solution the stopper of the separatory funnel should be held firmly in place and after shaking for a moment the stem of the funnel should be turned upward and the stop-cock opened to relieve any pressure within. Allow the liquids to separate in two layers, draw off the aqueous layer below, add some water and repeat the shaking and separation.

Ether is very volatile and mixtures of ether vapor and air are explosive, hence great care to avoid the neighborhood of flames must always be observed in working with ether. In distilling, efficient condensers fed with *cold* water should be used and the distillation must not be so rapid that vapors will escape from the lower end of the condenser.

Pour the washed ether from the top of the separatory funnel (why not draw it off below?) into a flask containing 10 to 15 grams of powdered calcium chloride. After some hours or on the following day filter the ether through a *dry* filter into a distilling bulb and distil from a water-bath which is not heated above 40°.

Ether prepared as above still retains small amounts of alcohol and of water. The alcohol can not be removed by washing with water. Metallic sodium in the form of wire will remove the water but after the water is removed its action on the alcohol is very slow. Magnesium bromide[1] will remove both alcohol and water very perfectly and absolute ether is best prepared in this manner. Allow the ether to stand for a day with some of the powdered magnesium bromide and distil. To the distillate add some fresh magnesium bromide and distil after three or four days, on a water-bath not heated above 40°. (L. W. Andrews, *loc. cit.*).

Ullmann recommends the removal of the alcohol and most of the water by shaking with 1/6 of its volume of sulphuric acid diluted with an equal volume of water. The ether may then be dried with sodium wire.

Pure ether boils at 34.6° and has a density at $15°/4° = 0.7191$ or at $25°/4° = 0.7079$.

Ether free from alcohol is not colored by shaking it with aniline violet, while a color is given to it, if alcohol is present.

The purity of the ether and the amount of alcohol present may also be determined by the index of refraction measured with a Pulfrich, inversion refractometer. For pure ether Andrews, gives, subject to revision, the values:

$$N_D \text{ at } 15° = 1.35514$$
$$N_D \text{ at } 20° = 1.35224$$
$$N_D \text{ at } 25° = 1.34933$$

One per cent. of alcohol increases the index of refraction at 25° to 1.34992, an increase of 0.00059.

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30. Preparation of an Ether from the Sodium Salt of a Phenol and Dimethyl Sulphate.—Anisole. Phenyl methyl ether, $C_6H_5 — O — CH_3$.

Literature.—Preparation from anisic acid, Cahours: Ann., 41, 68; 48, 65; 52, 327; 74, 298; From phenol, potassium hydroxide and methyl iodide, Cahours: Ann., 78, 227; From phenol, sodium hydroxide and dimethyl sulphate, Ullmann: Ann., 327, 114; Graebe: 340, 208; Ullmann: Organisch-Chemisches Pratikum, p. 160.

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[1] Prepared by mixing magnesium bromide with 4 or 5 per cent. of ammonium bromide, drying the mixture and heating till the ammonium bromide is expelled. The statements here given are from a paper on "The Manufacture of Absolute Ether," read before the Iowa Section of American Chemical Society at Grinnell, April 30, 1910.

18.8 grams phenol.
10 grams sodium hydroxide.
70 cc. water.
24 cc. dimethyl sulphate.

9 grams sodium hydroxide.
18.8 grams phenol.

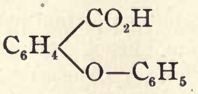
Under a hood with a good draft[1] mix in a 200 cc., not too thin, round-bottomed flask 18.8 grams of phenol, 10 grams of sodium hydroxide dissolved in about 70 cc. of water[2] and 24 cc. of dimethyl sulphate. Stopper and shake vigorously, removing the stopper from time to time to relieve the pressure and cooling, if necessary, to keep the temperature below 50°-60°. When the temperature no longer tends to rise, connect with an upright condenser and boil for a few minutes, adding more sodium hydroxide, if necessary to maintain an alkaline reaction. Cool and separate the solution of methyl sodium sulphate from the anisole (about 21 grams) by means of a separatory funnel.

To the aqueous solution add 9 grams of sodium hydroxide and 18.8 grams of phenol, connect with a condenser placed at an angle, since the mixture bumps badly, and boil for 6-7 hours. On account of the bumping both flask and condenser must be securely clamped. Add more sodium hydroxide, if necessary, to maintain an alkaline reaction.

Cool, separate the anisole as before, add it to the first portion, dry with calcium chloride, filter on a *dry* filter and distil. Yield 38 grams.

Anisole boils at 155° and has a specific gravity of 0.9878 at 21°/4°.

31. Preparation of an Ether from the Sodium Salt of a Phenol and an Aryl Halide with Metallic Copper as a Catalyzer. Phenol ether of salicylic acid,



$C_6H_4<\begin{matrix}CO_2H\\ O-C_6H_5\end{matrix}$.

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[1] Dimethyl sulphate is poisonous and breathing of its vapor must be carefully avoided.

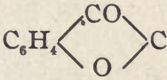
[2] It is very convenient to have in the laboratory a solution of sodium hydroxide of such strength that 3 cc. = 1 gram NaOH, for many purposes like this. 30 cc. of such a solution and 40 cc. of water would be used here.

Literature.—Use of copper as a catalyzer; Ullmann: Ber., 38, 2211; Ann., 355, 312; Preparation of phenol ether of chlorosalicylic acid, *Ibid*, 355, 366, 361; Preparation from *o*-diazonium benzoic sulphate and phenol, Griess: Ber., 21, 982; Preparation of phenylthiosalicylic acid, Goldberg: Ber., 37, 4526; Preparation of phenylanthranilic acid, Goldberg: Ber., 39, 1691; Of triphenylamine, Goldberg and Niemerovsky: Ber., 40, 2448.

1.53 gram sodium.
30 cc. methyl alcohol.

13 grams phenol.
5.1 grams *o*-chlorobenzoic acid.
0.1 gram copper powder.

In a 100 cc. flask dissolve 1.53 gram of sodium (2/30 mol.) in 30 cc. of absolute methyl alcohol. Add 13 grams of phenol and 5.1 gram (1/30 mol.) of chlorobenzoic[1] acid and expel the methyl alcohol at first on the water-bath and then by heating gently on an asbestos plate. Add 0.1 gram of copper powder and heat at 180° till the mass becomes solid. Cool, dissolve the mass in water with the addition of a little sodium carbonate, filter, extract the excess of phenol with ether, warm the aqueous solution for a short time in a porcelain dish or beaker to expel the ether, precipitate the phenyl ether of salicylic acid which has been formed with hydrochloric acid, filter it off and crystallize it from dilute alcohol.

The phenyl ether of salicylic acid crystallizes in leaflets which melt at 113°. It is converted quantitatively into xanthone,  $C_6H_4\left\langle\begin{matrix}CO\\O\end{matrix}\right\rangle C_6H_4$, by warming on the water-bath with concentrated sulphuric acid. (See 44, p. 105.)

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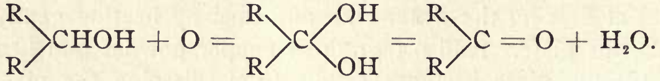
[1] This may be prepared by Sandmeyer's reaction (p. 201) from anthranilic acid. The yield is 70 to 80 per cent.

Chapter VI

ALDEHYDES, KETONES AND THEIR DERIVATIVES

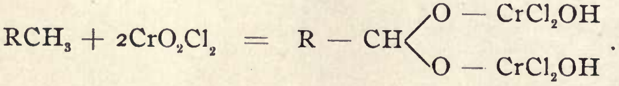
Aldehydes are prepared by the oxidation of primary, ketones by the oxidation of secondary alcohols, the oxidizing agent being, usually, potassium or sodium pyrochromate and dilute sulphuric acid, at moderate temperatures. Beckmann's mixture consisting of 60 grams (1 molecule) of potassium pyrochromate (or 54 grams of sodium pyrochromate), 50 grams (2.5 molecules) of concentrated sulphuric acid, and 300 cc. of water, is most generally suitable. (Ann., **250**, 325.)



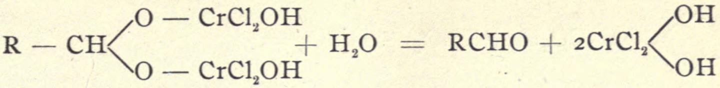
$$\left.\begin{matrix}R\\R\end{matrix}\right\rangle CHOH + O = \left.\begin{matrix}R\\R\end{matrix}\right\rangle C\left\langle\begin{matrix}OH\\OH\end{matrix}\right. = \left.\begin{matrix}R\\R\end{matrix}\right\rangle C = O + H_2O.$$

Aldehydes are prepared by distilling a mixture of a calcium or barium salt of an acid, with calcium or barium formate, ketones by distilling a calcium salt of an acid, or a mixture of calcium or barium salts. Bibasic acids, in which the two carboxyl groups are separated by four, five or six carbon atoms, give cyclopentanone, hexanone, or heptanone, and their derivatives by the same method. In most cases it is not necessary to prepare the calcium salt, but a mixture of the acid with a considerable excess of quicklime may be used instead. As with most pyrogenic reactions, the yields are considerably below the theoretical, and secondary reactions, causing the formation of alcohols and other products, take place.

In the aromatic series, aldehydes may be prepared by treating hydrocarbons with chromyl chloride, followed by water. The hydrocarbon and chromyl chloride are diluted with carbon bisulphide, and great care must be used to avoid accidents. (Étard: Ann. chim. phys. [5], **22**, 225; Bornemann: Ber., **17**, 1464.)

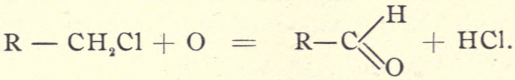


$$RCH_3 + 2CrO_2Cl_2 = R - CH\left\langle\begin{matrix}O - CrCl_2OH\\O - CrCl_2OH\end{matrix}\right..$$



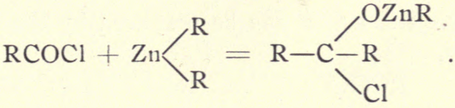
$$R - CH\begin{matrix} \diagup O - CrCl_2OH \\ \diagdown O - CrCl_2OH \end{matrix} + H_2O = RCHO + 2CrCl_2\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix}$$

Monochlor derivatives having the group CH_2Cl are often converted into aldehydes by boiling with an aqueous solution of some nitrate.

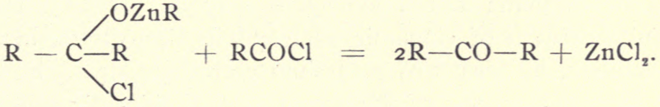


$$R - CH_2Cl + O = R-C\begin{matrix} \diagup H \\ \diagdown\!\!\diagdown O \end{matrix} + HCl.$$

Ketones are prepared by the action of chlorides of acids on zinc alkyls, or in the aromatic series, on hydrocarbons in the presence of aluminum chloride.

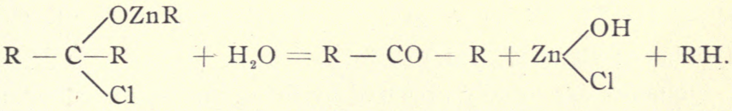


$$RCOCl + Zn\begin{matrix} \diagup R \\ \diagdown R \end{matrix} = R-\overset{\diagup OZnR}{\underset{\diagdown Cl}{C}}-R$$



$$R - \overset{\diagup OZnR}{\underset{\diagdown Cl}{C}}-R + RCOCl = 2R-CO-R + ZnCl_2.$$

or



$$R - \overset{\diagup OZnR}{\underset{\diagdown Cl}{C}}-R + H_2O = R - CO - R + Zn\begin{matrix} \diagup OH \\ \diagdown Cl \end{matrix} + RH.$$

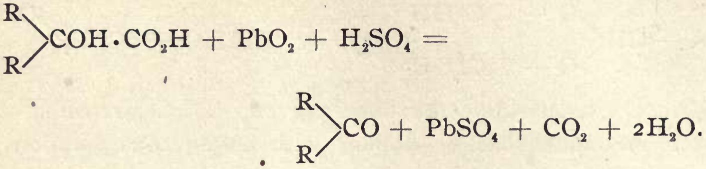
$$RH + RCOCl + AlCl_3 = R-CO-R + HCl + AlCl_3.$$

Practically, the use of zinc alkyl compounds has been displaced by the organomagnesium compounds as used in the Barbier-Grignard reaction (p. 67).

Ketones are prepared from acetoacetic ester and similar compounds by the "ketonic decomposition." (See p. 112.)

Aldehydes and ketones may be prepared by warming an α-hydroxy acid with lead peroxide and sulphuric acid. (Baeyer: Ber., **30**, 1962; Noyes and Shepherd: Am. Chem. J., **22**, 264.)

$$R-CHOHCO_2H + PbO_2 + H_2SO_4 = R-CHO + PbSO_4 + CO_2 + 2H_2O.$$



$$\begin{matrix}R\\R\end{matrix}\!\!>COH\cdot CO_2H + PbO_2 + H_2SO_4 = \begin{matrix}R\\R\end{matrix}\!\!>CO + PbSO_4 + CO_2 + 2H_2O.$$

The sodium salts of aliphatic nitro compounds are decomposed by acids with the formation of aldehydes or ketones. (Nef: Ann., 280, 267.)

$$2R{-}CH{=}NO{-}ONa + 2HCl = 2R{-}CHO + 2NaCl + N_2O + H_2O.$$

Many glyoxylic acids are decomposed by heat with the formation of aldehydes. (Bouveault: Bull. soc. chim. [3], 17, 363.) Glyoxylic acids may be prepared by the method of Verley, p. 107.

$$RCOCO_2H = R{-}CHO + CO_2.$$

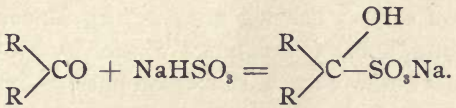
In the aromatic series, aldehydes may be prepared by the careful oxidation of cinnamic acid and its derivatives, in alkaline solution, by means of potassium permanganate. This is in some sense the reverse of the preparation of cinnamic acid from benzaldehyde.

$$R{-}CH{=}CH{-}CO_2H + 4O = R{-}CHO + 2CO_2 + H_2O.$$

(Einhorn: Ber., 17, 121.)

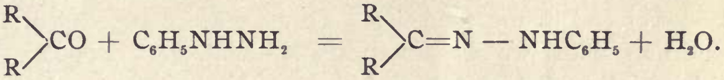
Quinones are usually prepared by the oxidation of aniline and its homologues, having a hydrogen atom, or a hydroxy or amino group in the para position to the amino group. Potassium or sodium pyrochromate and sulphuric acid are usually employed. In some cases, (*e. g.*, anthracene), a hydrocarbon can be oxidized directly to a quinone. The reaction in the case of compounds containing the amino group is complicated, and cannot be expressed by a simple reaction (see 27, p. 76).

Aldehydes and ketones are very reactive bodies, passing readily into alcohols and acids by reduction, or oxidation, and condensing very easily with a great variety of other substances, which makes them especially valuable for synthetical purposes. The most characteristic condensation products, and those most often used for purposes of identification and purification, because of their crystalline character, are the double compounds with acid sulphites of the alkali metals; the phenylhydrazones, (E. Fisher: Ber., **17**, 572; **21**, 984; **22**, 90); Oximes, (V. Meyer and Janny: Ber., **15**, 1324, 1525); And the semicarbazones, (Baeyer: Ber., **27**, 1918; Thiele and Stange: Ann., **283**, 1; Thiele and Heuser; *Ibid*, **288**, 311).



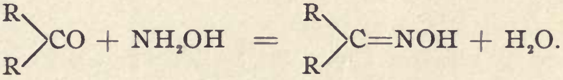
$$\begin{matrix}R\\R\end{matrix}{>}CO + NaHSO_3 = \begin{matrix}R\\R\end{matrix}{>}C{<}\begin{matrix}OH\\SO_3Na.\end{matrix}$$

Double compound with hydrogen sodium sulphite.



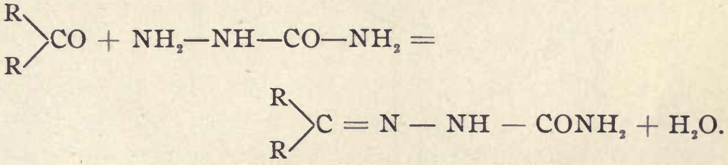
$$\begin{matrix}R\\R\end{matrix}{>}CO + C_6H_5NHNH_2 = \begin{matrix}R\\R\end{matrix}{>}C{=}N - NHC_6H_5 + H_2O.$$

Phenyl hydrazone



$$\begin{matrix}R\\R\end{matrix}{>}CO + NH_2OH = \begin{matrix}R\\R\end{matrix}{>}C{=}NOH + H_2O.$$

Oxime.



$$\begin{matrix}R\\R\end{matrix}{>}CO + NH_2{-}NH{-}CO{-}NH_2 = \begin{matrix}R\\R\end{matrix}{>}C = N - NH - CONH_2 + H_2O.$$

Semicarbazone.

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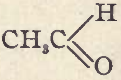
32. Preparation of an Aldehyde by Oxidation of a Primary Alcohol.—Acetaldehyde,  $CH_3C{<}\begin{matrix}H\\O\end{matrix}$ (Ethanal).

Literature.—Liebig: Ann., **14**, 133; Ritter: *Ibid*, **97**, 369; Städeler: Jahresb., 1859, 329; J. prakt. Chem., **76**, 54, (1859); Bourcart; Z. anal. Chem., **29**, 609; Rogers: J. prakt. Chem., **40**, 240, (1847); Weidenbusch: Ann., **66**, 152; Limpricht: *Ibid*, **97**, 369; Tollens: Ber., **14**, 1950; Orndorff and White: Am. Chem. J., **16**, 43.

150 grams (81 cc.) concentrated sulphuric acid.

300 cc. water.

100 grams sodium pyrochromate.
150 cc. water.
75 grams (95 cc.) alcohol.

Put in a one liter distilling bulb 300 cc. water, and 150 grams (81 cc.) of concentrated sulphuric acid. Dissolve 100 grams of sodium pyrochromate in 150 cc. of water, and add 75 cc. of alcohol. Put a stopper bearing a separatory funnel in the mouth of the distilling bulb, and connect a second 250 cc. distilling bulb to its side tube with a rubber stopper. Connect the side tube of the second bulb to a condenser which is directed upward, by running the side tube into a piece of rubber tubing drawn over the lower end of the condenser. Connect the upper end of the condenser with two wash-bottles fitted with cork stoppers, or with two Dreschel wash-bottles each containing about 25 cc. of dry ether. Surround the latter with a freezing mixture. Put the small distilling bulb into a dish containing water at 45°-50°, and feed the condenser with water at 30°. Heat the dilute sulphuric acid nearly to boiling, remove the flame, and drop in the pyrochromate mixture slowly. The reaction may proceed as rapidly as is possible without escape of aldehyde through the ether. Outside heating is not usually necessary after the reaction has commenced.

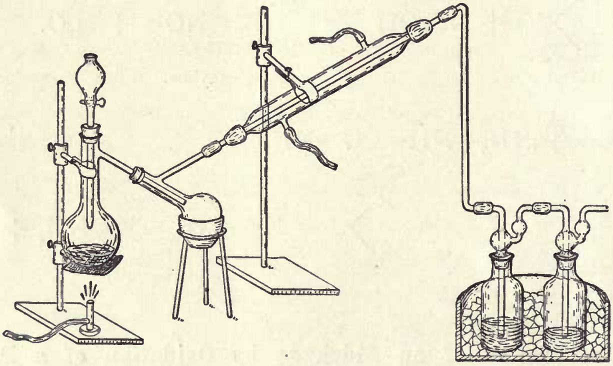
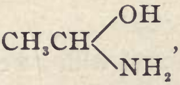


Fig. 28.

When all the mixture has been added and the aldehyde driven over, by heating for a short time, disconnect the wash-bottle, transfer the ethereal solution to a flask, set the latter in a freezing mixture, and pass in ammonia gas, generated by boiling strong aqua ammonia (0.90 sp. gr.), and dried by passing it over quicklime, or soda-lime in a drying cylinder. Use a wide delivery tube for the gas to prevent its being stopped by the aldehyde ammonia,  $CH_3CH\left<\begin{matrix}OH\\NH_2\end{matrix}\right.$, which is formed. Pass the gas till the solution smells strongly of ammonia, and allow the whole to stand for an hour. Filter off the crystals, and allow them to stand on filter paper for a short time. They can be kept for some time in tightly stoppered tubes or bottles, containing ammonia gas. Yield about 15 grams.

Aldehyde may be prepared from the crystals by dissolving them in their own weight of water, and dropping the solution into 4 parts of 50 per cent. sulphuric acid, condensing the aldehyde which is generated, with a condenser containing ice-water, and collecting in a flask surrounded with a freezing mixture.

Aldehyde boils at 21°, and has a specific gravity of 0.7951 at 10°. When warmed with caustic potash it is converted into a resin. It reduces a cold ammoniacal solution of silver nitrate (3 grams $AgNO_3$, 33 cc. NH_4OH, sp. gr. 0.90, 30 cc. 10 per cent. sodium hydroxide), a general reaction for aldehydes. It restores the color of a fuchsine solution which has been decolorized by sulphur dioxide. A drop of concentrated sulphuric acid converts it into paraldehyde, $C_6H_{12}O_3$, which melts at 10.5°, and boils at 124°. Hydrochloric acid gas converts it into a mixture of metaldehyde, $C_6H_{12}O_3$, and paraldehyde. Metaldehyde decomposes on standing, being converted partly into paraldehyde and partly into tetraldehyde, $C_8H_{16}O_4$. Paraldehyde and metaldehyde are probably stereomeric compounds. Orndorff and White, *loc. cit.*, Hantsch, however, Ber., **40**, 4341, considers metaldehyde as tetramolecular, $(C_2H_4O)_4$, or hexamolecular, $(C_2H_4O)_6$.)

33. Preparation of a Ketone by the Distillation of a Calcium Salt.—Acetone, (Propanone), CH_3COCH_3.

Literature.—Preparation from acetates, Liebig: Ann., **1**, 225; Dumas. Ann. chim. phys. (2), **49**, 208; By the dry distillation of wood, Völckel: Ann., **80**, 310; By the oxidation of citric acid, Pean: Jahresb., **1858**, 585; From acetyl chloride and zinc methyl, Freund: Ann., **118**, 11.

20 grams glacial acetic acid.
40 cc. water.
35 grams barium carbonate.

Mix 20 grams of glacial acetic acid with 40 cc. of water in a not too small porcelain dish, add in portions 35 grams of barium carbonate and evaporate the mixture rapidly to dryness on an asbestos plate, avoiding over heating after the water has been expelled. Put the dry residue in a hard glass tube 20 cm. long and 25-30 mm. in diameter. Connect with a condenser by means of cork stoppers and a bent glass tube and distil with a free flame, holding the burner in the hand to secure uniform heating of the whole mass.[1] Shake the distillate twice with 2-3 cc. of a concentrated solution of potassium carbonate to remove acids, dry with calcium chloride and distil from a small distilling bulb, using a water-cooled condenser and collecting the portion boiling at 54°-60°, in a *dry* weighed flask. Weigh the distillate and add to it 2½ times its weight of acid sodium sulphite dissolved in its own weight of warm water. When the double compound has completely separated, filter it off on a plate or a Hirsch funnel (p. 120) suck it as dry as possible, stop the pump moisten with a few drops of water, suck this off after a few minutes and repeat a second time. Dry the compound on a filter-paper.

Decompose one gram of the compound by mixing it with one gram of dry sodium carbonate and 10 cc. of water and distilling. Test the distillate with the iodoform reaction (p. 207).

Acetone boils at 56.5° and has a specific gravity of 0.7920 at 19.8°. It reacts readily with hypochlorites giving chloroform, or with hypobromites or hypoiodites giving bromoform or iodoform.

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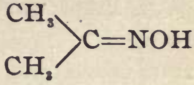
[1] Distillation from a small distilling bulb immersed in a bath of Wood's metal will give better yields.

34. Preparation of an Oxime.—Acetoxime,  $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C{=}NOH$ (Isonitroso acetone or propanone oxime).

Literature.—V. Meyer and Janny: Ber., **15**, 1324, 1529; Janny: *Ibid,* **16**, 170; V. Meyer and Wege: Ann., **264**, 121; Dodge: *Ibid,* **264**, 185; Beckmann: Ber., **21**, 767; Auwers: *Ibid,* **22**, 604.

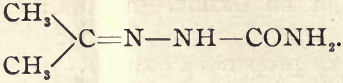
15 grams hydroxylamine hydrochloride.
14 grams (17 cc.) acetone.
8 grams sodium hydroxide.
50 cc. water.

Put in a 100 cc. glass stoppered bottle, 15 grams of hydroxylamine hydrochloride, and 17 cc. of acetone, and add a solution of 8 grams of sodium hydroxide in 50 cc. of water. Shake and cool somewhat, stopper tightly, and allow to stand for twenty-four hours. Extract the solution three times with about 20 cc. of ether, the ether being distilled off and used again each time, because of the volatility of the acetoxime. The last time distil only about one-half of the ether, transfer the remainder of the ethereal solution to a crystallizing dish, and allow the ether to evaporate spontaneously, or better *in vacuo* over sulphuric acid. As soon as the crystals are dry, transfer to a well stoppered bottle, as the substance is quite volatile. Yield 14 to 15 grams.

In the preparation of acetoxime, it is necessary to use the sodium hydroxide and hydroxylamine in equivalent amounts, as the acetoxime cannot be extracted from an acid or an alkaline solution. Auwers has shown, however, that in some cases the formation of an oxime is facilitated by using about three times the theoretical amount of sodium hydroxide.

Acetoxime crystallizes in prisms, which melt at 59°-60°. It boils at 134.8° under 728 mm. pressure. It is very easily soluble in water, alcohol, ether, and ligroïn. It can be extracted with ether only from neutral, not from acid, or alkaline solutions. It is decomposed by boiling with hydrochloric acid into acetone and hydroxylamine hydrochloride.

35. **Preparation of a Semicarbazone Compound.**—Semicarbazone of acetone,



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C{=}N{-}NH{-}CONH_2.$$

Literature.—Thiele and Stange: Ann., 283, 19; Thiele, Lachman and Heuser: *Ibid,* 288, 311; Baeyer: Ber., 27, 1918.

70 cc. concentrated sulphuric acid.
20 grams nitrate of urea.
Ice.

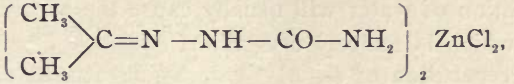
20 grams nitrourea.
150 cc. concentrated hydrochloric acid.
70 grams zinc dust.
Ice.

Salt.
20 grams sodium acetate.
12 grams acetone.

Put 70 cc. of concentrated sulphuric acid in a beaker and cool it below 0° with a freezing mixture. Add 20 grams of dry urea nitrate,[1] in small portions, stirring, and taking care that the mixture does not rise above 2°-3°. Allow to stand for half an hour, but not after there is much evolution of gas. Pour on such a quantity of ice that the temperature of the mixture is about 30°. Cool, filter, wash slightly, and suck as dry as possible. Stir in with 150 cc. of concentrated hydrochloric acid, previously cooled to 0°, and containing some pieces of ice. Pour in small portions, into a mixture of 70 grams of zinc dust, with powdered ice, keeping the whole in a beaker, or, especially in working with larger quantities in a granite iron dish, placed in a freezing mixture. The temperature should be kept at about 0°, but the use of much ice in the solution should be avoided, because of the resulting dilution. After all has been added, allow to stand for a short time, filter, add salt to saturation, and 20 grams of sodium acetate, and filter again, if necessary. These operations should be carried through rapidly, and the solution not allowed to become warm. Add 12 grams (15 cc.) of acetone, stir thoroughly, and allow to stand for some hours, if necessary over night, in a freezing mixture, or till the double compound of zinc with the acetone semicarbazone,

---

[1] This may be prepared as follows: Dissolve 12 grams of urea in 12 cc. of water, and pour the solution into 20 cc. of concentrated nitric acid, diluted with 20 cc. of water. Cool thoroughly, filter on a plate, and dry on filter paper, or porcelain. 20 to 22 grams should be obtained.



$$\left[{CH_3 \atop CH_3} > C{=}N-NH-CO-NH_2 \right]_2 ZnCl_2,$$

has separated as completely as possible. Filter off, wash with a little salt solution, and a little ice-water. 16 to 18 grams of the compound should be obtained.

By adding some benzaldehyde to the filtrate, stirring thoroughly, and allowing to stand, a small quantity of the semicarbazone of benzaldehyde can be obtained.

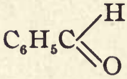
To obtain the acetone semicarbazone, digest 15 grams of the salt with 30 cc. of concentrated ammonia for some time, and filter.

To prepare the hydrochloride of semicarbazine, add to the acetone compound twice its weight of concentrated hydrochloric acid, and filter through a funnel loosely plugged with asbestos. Allow the solution to stand in a vacuum desiccator containing soda-lime and concentrated sulphuric acid, till it evaporates nearly to dryness. Dry the crystals of the chloride on porous porcelain.

Acetone semicarbazone crystallizes in needles, which melt with decomposition at 187°. It is moderately soluble in cold water, less soluble in alcohol, insoluble in ether. It reduces an ammoniacal silver solution immediately. It is easily decomposed by mineral acids, even in the cold.

The hydrochloride of semicarbazine, $NH_2CO—NH—NH_2—HCl$, crystallizes in prisms, which melt at 173° with decomposition. It dissolves very easily in water, less easily in hydrochloric acid, and is almost insoluble in alcohol, and ether. It is decomposed by heating with acids and alkalies. It condenses readily with most ketones and aldehydes, forming, usually, well crystallized compounds.

For the preparation of semicarbazones, Baeyer and Thiele recommend to dissolve the hydrochloride of semicarbazine in a little water, add the calculated amount of an alcoholic solution of potassium acetate and the ketone, and then alcohol and water to complete solution. The reaction is complete in a few minutes in some cases, in others it requires 4 to 5 days. When complete, the addition of water will usually cause the separation of a substance which is entirely crystalline.

36. Preparation of an Aldehyde by Treatment of a Monochlor Derivative of an Aromatic Hydrocarbon with a Nitrate.—Benzaldehyde,  $C_6H_5C\begin{smallmatrix}\diagup H\\ \diagdown\!\!\diagdown O\end{smallmatrix}$. (Oil of bitter almonds.)

Literature.—Liebig, Wöhler: Ann., 22, 1; Cannizzaro: *Ibid,* 88, 129; Dumas, Peligot: *Ibid,* 14, 50; Guckelberger: *Ibid,* 64, 60; 72, 86; Lauth, Grimaux: Bull. soc. chim., 7, 106; Piria: Ann., 100, 105; Limpricht: *Ibid,* 139, 319; Anschütz: *Ibid,* 226, 18.

40 grams benzyl chloride.
40 grams barium nitrate.
300 cc. water.

Put in a 500 cc. round-bottomed flask 40 grams of benzyl chloride, 40 grams of barium nitrate (or 30 grams of calcium nitrate, prepared by treating an excess of calcium carbonate with the theoretical amount of nitric acid, and filtering), and 300 cc. of water. Connect with an upright condenser, best with a rubber tube slipped over the neck of the flask, the condenser reaching well down into the neck of the latter, so that the nitrous fumes evolved will come but little in contact with the rubber. The connection must be tight. Put in the top of the condenser a rubber stopper bearing a tube, which reaches down into the liquid, and also a tube which will convey the gases coming from the condenser to the bottom of a 150 cc. bottle, or, better, of a large tube, closed below. Pass through the first tube a slow current of carbon dioxide, and boil the contents of the flask gently, on a wire gauze, for six or eight hours, or till the odor of the benzyl chloride nearly, or quite disappears. Some such means as that described for the exclusion of the air is essential to prevent the oxidation of the aldehyde to benzoic acid.

Extract the benzaldehyde with ether, distil off the latter, and shake the residue with three or four times its volume of a strong solution of acid sodium sulphite,[1] in a stoppered bottle. After some time, filter off the bisulphite compound and wash successively with a very little water, alcohol, and ether. Put the compound in a distilling bulb with an excess of a strong solution of sodium carbonate, and distil with steam. Extract the benzaldehyde from the distillate with ether, dry with calcium chloride, and distil. Yield 10 to 15 grams.

Benzaldehyde melts at—13°.5 and boils at 179°. It has a specific gravity of 1.0504 at 15°. It oxidizes slowly on standing in the air, when pure. It is more stable when it contains hydrocyanic acid, which is usually added to the commercial article for this reason. It dissolves in 300 parts of water, but is easily soluble in alcohol, and ether.

37. Condensation of an Aldehyde with Itself by Means of Potassium Cyanide.—Benzoïn, $C_6H_5CHOHCOC_6H_5$.

Literature.—Liebig and Wöhler: Ann., 3, 276; Brewer, Zincke: *Ibid,* 198, 151; Päpcke: Ber., 21, 1335; A. Smith and Ransom: Am. Chem. J., 16, 108.

20 grams benzaldehyde.
2 grams potassium cyanide.
50 cc. alcohol.
40 cc. water.

Boil the mixture given above with an upright condenser for half an hour. Cool, filter, wash with dilute alcohol, and crystallize from a little hot alcohol. A little more benzoïn may be obtained by adding a little more potassium cyanide to the filtrate, and boiling again for a quarter of an hour. Yield 15 to 18 grams.

Benzoïn melts at 134°, and boils with some decomposition at 320°. By warming on the water-bath for two hours with two and one-half times its weight of nitric acid (sp. gr. 1.33), with frequent shaking, it is oxidized to benzil, $C_6H_5COCOC_6H_5$.

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[1] This must be freshly prepared by passing sulphur dioxide into a mixture of acid sodium carbonate with three parts of water, till the solution smells strongly of the gas For sulphur dioxide, see p. 78.

By means of fuming hydriodic acid benzoïn may be reduced to dibenzyl, $C_6H_5CH_2CH_2C_6H_5$.

38. **Oxidation of a Secondary Alcohol to a Ketone.**—Benzil, $C_6H_5—COCO—C_6H_5$.

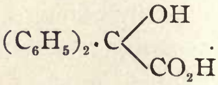
Literature.—Preparation from benzoin, Zinin: Ann., 34, 188; Preparation from 1.2-diphenyltetrachlorethane, (tolantetrachloride) and color reactions with alcoholic potash: Liebermann and Homeyer: Ber., 12, 1975; Rearrangement to diphenyl glycolic acid (benzilic acid), Liebig: Ann., 25, 27; Zinin: Ann., 31, 329; Staudinger: Ann., 356, 71; Condensation with orthodiamines to a quinoxaline, Hinsberg: Ann., 237, 327; Hinsberg and König: Ber., 27, 2181; Condensation with ammonia and aldehydes to glyoxalines, Radziszewski: Ber., 15, 1494, 2706; Preparation, Henle, Anleitung für das organisch preparative Praktikum, p. 143.

10 grams benzoïn.

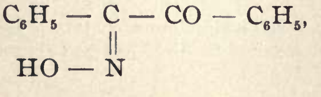
25 cc. nitric acid (1.42).

Put in a small flask 10 grams of benzoïn and 25 cc. of concentrated nitric acid, (sp. gr. 1.42). Heat on the water-bath with frequent shaking till oxides of nitrogen are no longer evolved and a few drops of the solution give, on dilution, a precipitate which after washing and dissolving in alcohol does not reduce Fehling's solution. Precipitate with water, filter on a plate, wash and recrystallize from alcohol. Yield 9 grams.

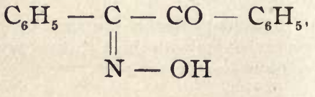
Benzil crystallizes from ether in prisms which melt at 95°. It boils at 346°-348°, with some decomposition, under atmospheric pressure or at 188° under a pressure of 12 mm. or at 104°-105° under a high vacuum.

When fused with caustic potash and a little water benzil rearranges to diphenylglycolic acid (benzilic acid)  $(C_6H_5)_2\cdot C\begin{matrix}OH\\CO_2H\end{matrix}$.

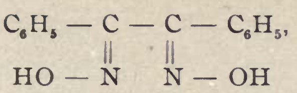
Benzil has been of unusual interest, because of the part which its compounds have played in the development of the theories of stereo-chemistry. It forms two monoximes and three dioximes, to which the following stereomeric formulas have been given:



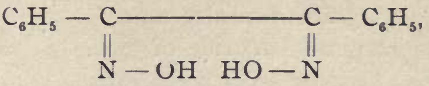
$$\begin{matrix}C_6H_5 - & C & - CO - C_6H_5,\\ & \| & \\ HO - & N & \end{matrix}$$



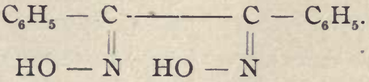
$$\begin{matrix}C_6H_5 - & C & - CO - C_6H_5,\\ & \| & \\ & N & - OH\end{matrix}$$



$$\begin{array}{llll} C_6H_5 - & C - & C - & C_6H_5, \\ & \| & \| & \\ HO - & N & N - & OH \end{array}$$



$$\begin{array}{llll} C_6H_5 - & C \text{———————} & C - & C_6H_5, \\ & \| & \| & \\ & N - OH & HO - N & \end{array}$$



$$\begin{array}{llll} C_6H_5 - & C \text{———} & C - & C_6H_5. \\ & \| & \| & \\ HO - & N & HO - N & \end{array}$$

Some have supposed that the differences are due to structural isomerism and not to stereoisomerism. See Wittenberg and V. Meyer: Ber., **16**, 503; Auwers and V. Meyer: *Ibid,* **21**, 784, 3510; **22**, 537, 564, 1985, 1996; Hantsch and Werner: *Ibid,* **23**, 11, 1243.

39. **Condensation of an Aldehyde with a Ketone and Oxidation of the Acetyl Group with Sodium Hypochlorite.**—Cinnamic acid, $C_6H_5CH = CHCO_2H$.

Literature.—See preparation of cinnamic acid p. 133, also Engler, Leist: Ber., **6**, 254, 257; Claisen, Claparède: *Ibid,* **14**, 2461; Claisen, Ponder: Ann., **223**, 139; J. G. Schmidt: Ber., **14**, 1460; Meister, Lucius and Brüning, D. R. P., 21162, *Ibid,* **16**, 449; Vorlander: Ber., **30**, 2261, Ann., **294**, 275; Straus, Caspari: Ber., **40**, 2698. Foot note 4.

10 grams benzaldehyde.
25 cc. acetone.
10 cc. caustic soda (10 per cent.).
900 cc. water.

In a one liter flask place 900 cc. of water, 10 grams of benzaldehyde, 25 cc. acetone and 10 cc. of caustic soda, free from carbonate. Mix thoroughly by shaking and allow to stand for four days, shaking occasionally. The aldehyde and acetone condense with the formation of benzalacetone, $C_6H_5—CH=CHCOCH_3$, and dibenzalacetone, $C_6H_5—CH=CH—CO—CH=CH—C_6H_5$. Add 200 grams of salt (see 74, p. 167) and filter off and wash the dibenzalacetone if it is solid, or extract twice with a small amount of ether, if it is liquid. Distil off the ether and fractionate the benzalacetone from a small distilling bulb (see Fig. 34, p. 171), under diminished pressure. The benzalacetone distils at 151°-153° under 25 mm. pressure, at 260°-262° under 760 mm., and melts at 42°.

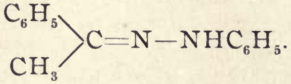
2.5 grams benzalacetone.
12 grams chloride of lime.
15 grams sodium carbonate.
125 cc. water.

To 12 grams of chloride of lime (containing 31 per cent. of available chlorine) add 50 cc. of water and 75 cc. of a solution of sodium carbonate (5 cc. = 1 gram Na_2CO_3). Filter with the pump and wash once. To the filtrate add 2.5 grams of benzalacetone, warm to 80°-90° and shake vigorously. Continue to warm and shake till the odor of chloroform is no longer apparent. The benzalacetone should now have passed into solution.

Cool, filter, precipitate the cinnamic acid with sulphuric acid and recrystallize from hot water. The oxidation is exactly analogous to that by which chloroform is prepared commercially from acetone. For the properties of cinnamic acid see p. 134.

The condensation of benzaldehyde with a methyl or methylene group adjacent to carboxyl is a quite general reaction and may sometimes furnish a basis for the determination of the structure of compounds. See Noyes and Shepherd: Am. Chem. J., **22**, 265.

40. Preparation of a Phenylhydrazone.—Phenylhydrazone of acetophenone,



$$\left.\begin{array}{l}C_6H_5\\CH_3\end{array}\right>C{=}N{-}NHC_6H_5.$$

Literature.—E. Fischer: Ber., **17**, 573; **22**, 90; **16**, 2241; Overton: *Ibid*, **26**, R 18, Reisenegger. *Ibid*, **16**, 661.

5 cc. acetic acid (30 per cent.).
1.5 cc. phenyl hydrazine.
1 cc. acetophenone.

Dissolve 1.5 cc. of phenyl hydrazine in 5 cc. of acetic acid (30 per cent.) in a test-tube, add 1 cc. of acetophenone, and shake vigorously till the hydrazone separates in crystalline form. Filter, wash with water, dissolve in a very small beaker, in a little hot alcohol, add water till the hot solution begins to grow turbid, and allow to crystallize.

The hydrazone of acetophenone is very easily obtained and purified. In some cases, where there is difficulty in obtaining a crystalline product, Overton (*loc. cit.*) recommends to dissolve the ketone in a little glacial acetic acid, add a slight excess of phenyl hydrazine, and allow the mixture to stand in the cold till the hydrazone separates.

Acetophenone phenylhydrazone crystallizes from dilute alcohol in leaflets, which melt at 105°. It is decomposed by concentrated hydrochloric acid into phenyl hydrazine hydrochloride, and acetophenone. By sodium amalgam, in alcoholic solution, it is reduced to a mixture of aniline and phenyl methyl carbinamine, $C_6H_5CHNH_2CH_3$ (1^1-aminoethylphen).

41. **Preparation of a Ketone by Condensation of an Acid Chloride with Benzene by Means of Aluminium Chloride.**—Benzophenone, $C_6H_5COC_6H_5$. (Diphenylmethanone.)

Literature.—Peligot: Ann., 12, 41; Chancel: *Ibid*, 72, 279; Otto: Ber., 3, 197; Friedel, Crafts: Ann. chim. phys., [6], 1, 510, 518; Zincke: Ann., 159, 377; Friedel, Crafts, Ador: Ber., 10, 1854; Stockhausen and Gattermann: Ber., 25, 3521; Radziewanowski: *Ibid*, 27, 3235; 28, 1135; Crafts: Am. Chem. J., 5, 324; Preparation by use of ferric chloride, Nencke and Stoeber: Ber., 30, 1768.

20 grams benzene.
20 grams benzoylchloride.
100 grams carbon disulphide.
20 grams aluminium chloride.

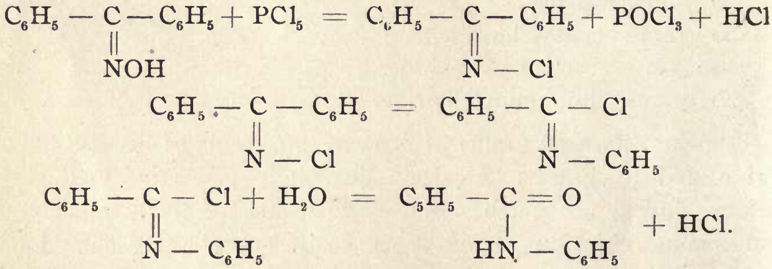
Put in a flask 20 grams of benzene, 20 grams of benzoyl chloride, and 100 grams of carbon disulphide. Add in small portions, during about ten minutes, 20 grams of finely powdered aluminium chloride. (See 16, p. 59.) The chloride should be exposed to the air as little as possible. Connect with a reversed condenser, and heat on the water-bath for two to three hours, or till the evolution of hydrochloric acid nearly ceases. Distil off the carbon disulphide, and pour the residue into 300 cc. of water in a flask, cooling, if necessary. Add 10 cc. of concentrated hydrochloric acid, and pass a rapid current of steam through the liquid for a short time to expel the rest of the benzene and carbon disulphide. Collect the benzophenone with some ether, separate, wash the ethereal solution by shaking it several times with water, and with a solution of sodium hydroxide, dry it with calcium chloride, and fraction the residue, after distilling off the ether, using a distilling bulb, and collecting the distillate directly in a test-tube, or preparation tube, without using a condenser. Yield 20 to 21 grams.

Benzophenone melts at 48.5°, and boils at

303.7°	under	723.05	mm.
304.5°	"	735.45	"
305.5°	"	750.91	"
306.1°	"	760.32	"
306.4°	"	765.06	"

This table is of especial value for testing thermometers. (See p. 28.)

When benzophenone is warmed with hydroxylamine hydrochloride, caustic soda in excess, and alcohol, for two hours, an oxime melting at 140° is formed. If this oxime dissolved in dry ether, is treated successively with one and a half times its weight of phosphorus pentachloride, and with water, it is converted into benzanilide (Beckmann's rearrangement).

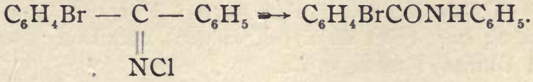


$$C_6H_5 - \underset{\underset{NOH}{\|}}{C} - C_6H_5 + PCl_5 = C_6H_5 - \underset{\underset{N - Cl}{\|}}{C} - C_6H_5 + POCl_3 + HCl$$

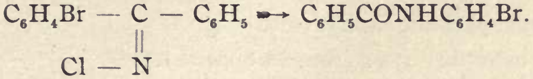
$$C_6H_5 - \underset{\underset{N - Cl}{\|}}{C} - C_6H_5 = C_6H_5 - \underset{\underset{N - C_6H_5}{\|}}{C} - Cl$$

$$C_6H_5 - \underset{\underset{N - C_6H_5}{\|}}{C} - Cl + H_2O = C_5H_5 - \underset{\underset{HN - C_6H_5}{|}}{C} = O + HCl.$$

The study of this reaction has been of great value in the development of theories about the stereochemistry of nitrogen. Unsymmetrical oximes which occur in two forms, as, for instance, monobrombenzophenone oxime, $C_6H_4Br\underset{\underset{NOH}{\|}}{C}C_6H_5$, may be rearranged in this manner, and each form gives a different product: viz., brombenzoylanilide and benzoylbromanilide.



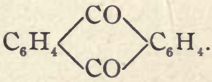
$$C_6H_4Br-\underset{\underset{NCl}{\|}}{C}-C_6H_5 \longrightarrow C_6H_4BrCONHC_6H_5.$$



$$C_6H_4Br-\underset{\underset{Cl-N}{\|}}{C}-C_6H_5 \longrightarrow C_6H_5CONHC_6H_4Br.$$

The two compounds can be distinguished by their saponification products.

42. Oxidation of a Hydrocarbon to a Quinone.—Anthraquinone,



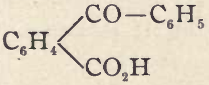
Literature.—Laurent, Berzelius: Jahresb., 16, 366; Anderson: Ann., 122, 301; Kekulé, Franchimont: Ber., 5, 908; Ullmann: Ann., 291, 24; W. H. Perkin, Jr.: J. Chem. Soc., 59, 1012; Graebe, Liebermann: Ann. Supl., 7, 285.

10 grams anthracene.
17 grams chromic anhydride.
100 cc. glacial acetic acid.

Put 10 grams of anthracene, and 75 cc. glacial acetic acid in a flask connected with an upright condenser, heat to boiling, and add, slowly, 17 grams of chromic anhydride, dissolved in the smallest possible amount of water, and the solution diluted with 25 cc. glacial acetic acid. Boil for five to ten minutes, pour the solution into water, filter, and wash. Dry the residue, and crystallize it from glacial acetic acid, or from toluene. It may also be purified by sublimation (see p. . .). Yield almost quantitative, if the anthracene is pure.

Anthraquinone sublimes in yellow needles, which melt at 273°, and boil at 379°-381°. 100 parts of toluene dissolve 0.19 parts at 15°, and 2.56 parts at 100°. By distilling with zinc dust anthracene is regenerated.

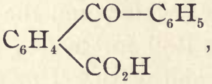
43. Preparation of a Derivative of a Ketone by Condensation of Phthalic Anhydride with a Hydrocarbon.—Orthobenzoylbenzoic Acid,



, Diphenylmethanonemethyllic (2) acid.

Literature.—Plaskuda, Zincke: Ber., 6, 707; Behr, vanDorp: *Ibid,* 7, 17; Friedel, Crafts: Ann. chim. phys. [6], 14, 446; Pechmann: Ber., 13, 1612; Graebe and Ullmann: Ann., 291, 8.

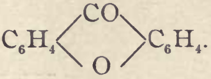
20 grams phthalic anhydride.
100 cc. benzene (free from thiophene).
30 grams aluminium chloride.

In a 300 cc. flask put 20 grams of phthalic anhydride, and 100 cc. of benzene, free from thiophene. Warm till the anhydride dissolves, and cool. Connect with an upright condenser, and add, in portions of 3-5 grams, 30 grams of dry, powdered aluminium chloride. If the reaction becomes too violent, cool the flask with water. The whole of the chloride may be added in ten to fifteen minutes. Warm on the water-bath for two hours. Cool, add carefully, through the condenser, 80 cc. of cold water, and 20 cc. of concentrated hydrochloric acid. Distil off the benzene with water vapor, cool, filter, and wash. Dissolve the acid in 80 cc. of a 10-per cent., solution of sodium carbonate, filter, and pour into a mixture of 35 cc. of concentrated hydrochloric acid, 40 cc. of water, and some pieces of ice. Filter, and suck dry on a plate (p. 120). In order to obtain the dry *o*-benzoylbenzoic acid,  $C_6H_4\langle{}^{CO-C_6H_5}_{CO_2H}$, this product may be dried at 125°-130°, or it may be dissolved in warm chloroform, separated from the water swimming on top, the solution dried with calcium chloride, and the chloroform distilled. The dry acid may be crystallized from xylene. Yield 22 to 23 grams.

Orthobenzoylbenzoic acid crystallizes from water in long needles, which contain water of crystallization and melt at 85°-87°. It is moderately soluble in hot water, difficultly soluble in cold water.

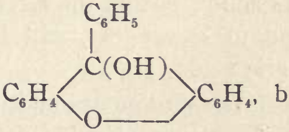
When the dry acid is heated to 200°, for an hour, with an equal weight of phosphorus pentachloride, it is converted almost quantitatively into anthraquinone.

44. Preparation of a Ketone Ether by the Condensing Action of Sulphuric Acid.

—Xanthone,  $C_6H_4\left\langle {CO \atop O} \right\rangle C_6H_4$.

Literature.—Preparation by the oxidation of methylene diphenyleneketone oxide, Mertz, Weith: Ber., 14, 192; From 2.2′diaminobenzophenone with nitrous acid, Staedel: Ann., 283, 175; From salicylic acid and acetic anhydride, W. H. Perkin: Ber., 16, 339; Richard Meyer and Hoffmeyer: Ber., 25, 2118; By warming salicylic phenyl ether with sulphuric acid, Graebe: Ber., 21, 503.

3 grams phenyl ether of salicyclic acid.
20 cc. concentrated sulphuric acid.

Put 3 grams of the phenyl ether of salicyclic acid (31, p. 84) and 20 cc. of concentrated sulphuric acid in a small flask, heat for half an hour on the water-bath, cool, pour into about 200 cc. of water, filter off and wash the precipitated xanthone and recrystallize it from hot alcohol, or, after drying, from benzene. Xanthone crystallizes in needles which melt at 173°-174°. It dissolves in concentrated sulphuric acid with a yellow color and intensive blue fluorescence. It may be readily converted into phenyl xanthenol,  $C_6H_4\left\langle {\overset{C_6H_5}{\overset{|}{C(OH)}} \atop O} \right\rangle C_6H_4$, by the Barbier-Grignard reaction, Gomberg and Cone: Ann., 370, 173. (See also p. 74.)

Instead of concentrated sulphuric acid phosphorus pentachloride (to form the acid chloride) followed by aluminium chloride, (see 41, p. 101) may be used. For naphthalene derivatives this is essential because of the ease with which they are sulphonated. Ullmann: Ann., 355, 349.

Chapter VII

ACIDS

I. *Oxidation of Alcohols, Aldehydes, Ketones, and Hydrocarbons.*—The oxidation is usually effected by a mixture of potassium pyrochromate, sulphuric acid, and water, by dilute nitric acid, or by potassium permanganate in alkaline solution.

With the chromic acid mixture the first product of the oxidation of an alcohol is probably an aldehyde or ketone. In the case of ethyl alcohol the aldehyde is so volatile as to escape rapidly as soon as formed and the method cannot be practically used for the preparation of acetic acid.

With some of the higher alcohols of the same series the acid which is formed by the oxidation of a part of the alcohol combines with another portion of the alcohol to form an ester. The continued action of the oxidizing mixture may saponify the ester and complete the oxidation of the alcohol, but it is sometimes better to moderate its action so that the ester is the chief product of the oxidation and to secure the acid by the saponification of the latter (isovaleric acid).

The oxidation of open chain ketones and of secondary alcohols can give rise to the formation of acids only by separating the molecule into two parts. The carbonyl of the ketone usually, but not always, goes with the smaller part. There may result a single acid, as in the case of methyl ethyl ketone (2-butanone), or two acids, as with dipropyl ketone (4-heptanone or propyl methyl ketone (2-pentanone). In the latter case, for purposes of investigation, the separation of homologous fatty acids becomes important. This can be effected by distilling an aqueous solution of the acids. The acid of higher molecular weight passes over first with the water vapor, apparently because it is less soluble in water and because of its lower ionization constant, as the portion of an acid which is ionized can pass over only to a trifling extent, if at all, with steam. By preparing silver salts of the acids in the first and last portions of the distillate the composition of the acids formed can be established. (See **47**, p. 119), separation of propionic and butyric acids.)

The oxidation of cyclic ketones, and in some cases of other cyclic compounds, gives rise to the formation of bi-basic acids (camphoric acid).

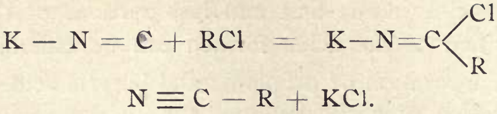
In the benzene series, a side chain consisting of allyl (CH_3, C_2H_5, etc.) or another group in which a carbon atom is combined directly with the benzene nucleus, can be oxidized to carboxyl. In the case of hydrocarbons, the oxidation is usually effected with difficulty, partly owing to their insolubility in the oxidizing agents employed. On this account it is sometimes advisable to prepare, at first, a halogen derivative having the halogen in the side chain (Baeyer: Oxidation of paraxylene, Ann. **245**, 138; benzoic acid, p. 125).

In a similar manner an acetyl group, $COCH_3$, may be converted to the group $COCH_2Br$ by treatment with bromine in a solution in carbon bisulphide and the latter may be oxidized to the glyoxylic group, $COCO_2H$, by shaking with a cold, 5 per cent. solution of potassium permanganate. (Verley: Bull. soc. chim., **17**, 906.) The glyoxylic group is converted into the aldehyde group, in some cases, by heat (p. 88) or it may be oxidized to carboxyl by means of manganese dioxide and sulphuric acid.

The acetyl group may be oxidized to carboxyl with the simultaneous formation of chloroform or bromoform by means of sodium hypochlorite or hypobromite. (See **39**, p. 99.)

II. *Saponification of Cyanides.*—The cyanides of organic radicals, or "nitriles" of acids, may be obtained from halogen derivatives of hydrocarbons, salts of acid sulphuric esters of alcohols, or salts of sulphonic acids by treating with potassium cyanide. The last two cases are applicable only when the cyanide formed can be distilled from the dry mixture without decomposition.

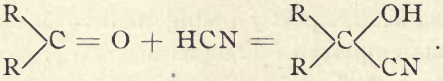
Nef has shown that potassium cyanide has the structure K—N = C, and the reaction probably takes place in two stages:



$$K-N=C+RCl = K-N=C\left\langle\begin{matrix}Cl\\R\end{matrix}\right.$$
$$N\equiv C-R+KCl.$$

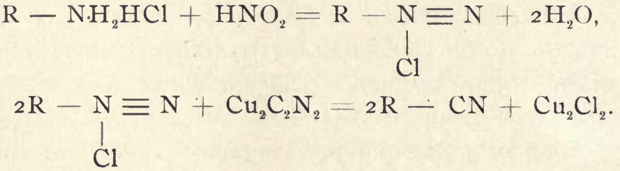
A small amount of an isocyanide is formed at the same time, the group — N = C taking the place of the halogen or acid group of the organic compound.

Cyanhydrines, which by saponification give α-hydroxy acids, can be prepared by treating aldehydes or ketones with hydrocyanic acid, best in the nascent state:



$$\left.\begin{matrix}R\\R\end{matrix}\right\rangle C=O+HCN=\left.\begin{matrix}R\\R\end{matrix}\right\rangle C\left\langle\begin{matrix}OH\\CN\end{matrix}\right. .$$

From aromatic amines cyanides can be obtained by treating a diazonium salt with cuprous cyanide. (Sandmeyer.)



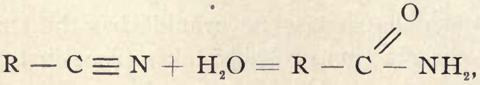
$$R-NH_2HCl+HNO_2=R-\underset{\displaystyle Cl}{\underset{|}{N}}\equiv N+2H_2O,$$

$$2R-\underset{\displaystyle Cl}{\underset{|}{N}}\equiv N+Cu_2C_2N_2=2R-CN+Cu_2Cl_2.$$

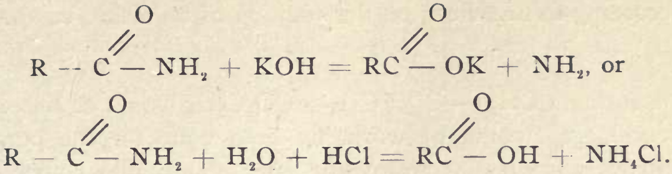
The cuprous cyanide for the reaction is prepared from copper sulphate.

$$CuSO_4+2KCN=Cu(CN)_2+K_2SO_4,$$
$$2Cu(CN)_2=Cu_2(CN)_2+(CN)_2.$$

The saponification of cyanides is usually effected either by the action of an aqueous or alcoholic solution of potassium, sodium, or barium hydroxide, or by the action of hydrochloric or sulphuric acid. An amide of the organic acid is probably always an intermediate product of the saponification and, in some cases, the conversion of the cyanide into an amide and the conversion of the latter into the acid may, with advantage, be carried out in two stages and by means of different agents.



$$R-C\equiv N+H_2O=R-\overset{\displaystyle O}{\overset{/\!/}{C}}-NH_2,$$



$$R - \overset{O}{\overset{/\!/}{C}} - NH_2 + KOH = R\overset{O}{\overset{/\!/}{C}} - OK + NH_2,\text{ or}$$

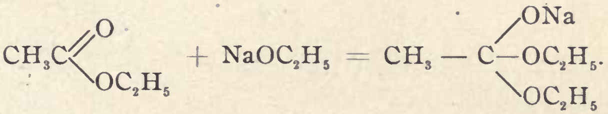
$$R - \overset{O}{\overset{/\!/}{C}} - NH_2 + H_2O + HCl = R\overset{O}{\overset{/\!/}{C}} - OH + NH_4Cl.$$

III. *Condensation.*—By condensation, in general, is meant the formation of a compound from two others with the elimination of water, alcohol, ammonia, hydrochloric acid, or two halogen atoms.[1] Methods of condensation have been especially useful in the synthesis of acetoacetic ester and its derivatives, of cinnamic acid, and of many other compounds in which the same principles have been applied.

In the case of acetoacetic ester the condensation appears to take place as follows:

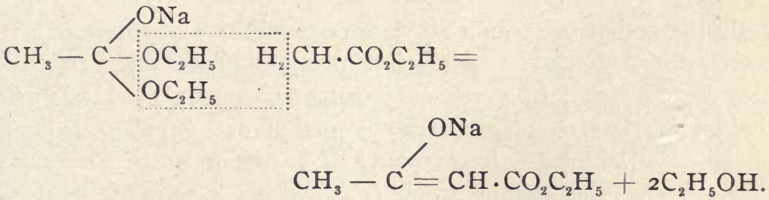
$$CH_3CO \cdot \boxed{OC_2H_5 + H}CH_3CO_2C_2H_5 = CH_3COCH_2CO_2C_2H_5 + C_2H_5OH.$$

The researches of Claisen indicate, however, that the action consists, at first, in the addition of sodium ethylate, formed from a trace of alcohol which is always present in acetic ester, to the ester, thus:



$$CH_3C\begin{smallmatrix}/\!/O \\ \diagdown OC_2H_5\end{smallmatrix} + NaOC_2H_5 = CH_3 - C\begin{smallmatrix}/ONa \\ -OC_2H_5. \\ \diagdown OC_2H_5\end{smallmatrix}$$

The addition product then condenses with a second molecule of acetic ester thus:



$$CH_3 - C\begin{smallmatrix}/ONa \\ -\boxed{OC_2H_5 \quad H_2} \\ \diagdown OC_2H_5\end{smallmatrix}CH \cdot CO_2C_2H_5 =$$

$$CH_3 - \overset{ONa}{\overset{/}{C}} = CH \cdot CO_2C_2H_5 + 2C_2H_5OH.$$

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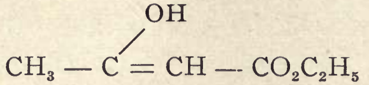
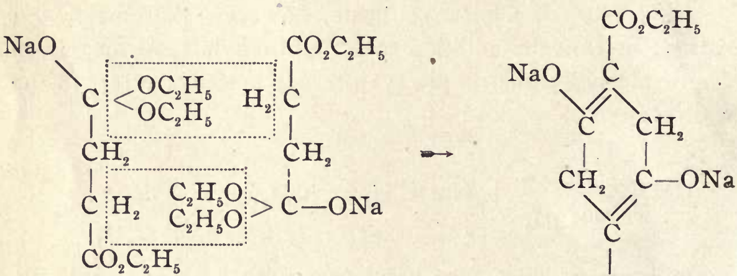
[1] Some authors use the term condensation exclusively as applied to reactions in which carbon atoms unite, and especially with the elimination of water or alcohol, but there appears to be no logical reason for such a restriction in its use.



According to this view, on the addition of an acid a compound of the formula $CH_3 - \overset{OH}{\overset{/}{C}} = CH - CO_2C_2H_5$ would be liberated. A very large amount of work has been done for the purpose of discovering whether acetoacetic ester and similar compounds have the "enol" (unsaturated alcoholic) or ketone structure. It would seem that substances of this character pass very readily from one form into the other and that while, in some cases, they may consist exclusively of the one or the other form, in others they are, in all probability, mixtures of the two forms. Therefore the compounds in question may react in one or the other form or in both, according to the reagents used, one form passing over into the other, as the one or other form disappears in the progress of the reaction.

Very closely analogous to the preparation of acetoacetic ester is the preparation of succinylosuccinic ester by the condensation of succinic ester.

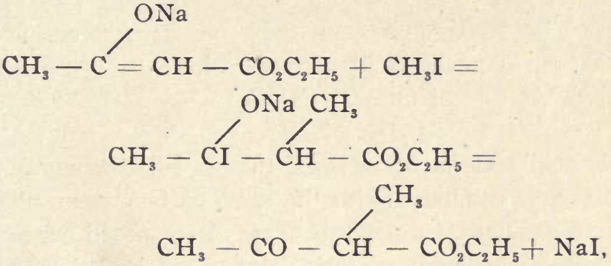


Succinic ester + sodium ethylate.

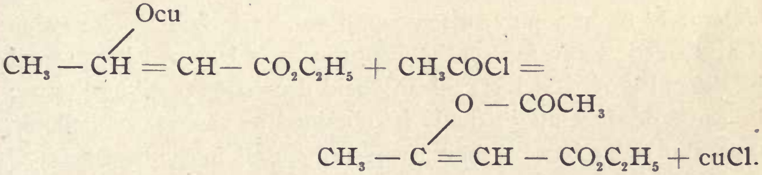
Sodium salt of succinylosuccinic ester.

By the action of sodium ethylate on a mixture of esters or of esters and ketones or aldehydes, many similar condensations may be effected. In every case one ester group, after adding sodium ethylate, condenses with a methyl or methylene group which is adjacent to the carbonyl of a ketone or of an ester group. That the methin group (CH) is not susceptible to this sort of condensation is one of the proofs for Claisen's view, referred to above (Ber., **20**, 651; **21**, 1154).

Acetoacetic ester and similar compounds which contain a methylene or methin group between two carbonyl or ester groups give sodium salts when treated with sodium ethylate. In some cases cyanogen or other groups may have the same effect as carbonyl. According to the view now most generally held, the sodium is combined with oxygen in these sodium salts ("enol" form, see above), though some chemists formerly supposed that it is combined with carbon (ketone form). When these sodium, silver, or copper salts of acetoacetic ester, malonic ester, and similar compounds are treated with alkyl iodides, acid chlorides, or other halogen derivatives, compounds are formed in which the alkyl or other groups are sometimes combined with carbon and sometimes with oxygen.



$$CH_3-\overset{ONa}{C}=CH-CO_2C_2H_5+CH_3I= \\ CH_3-\overset{ONa}{CI}-\overset{CH_3}{CH}-CO_2C_2H_5= \\ CH_3-CO-\overset{CH_3}{CH}-CO_2C_2H_5+NaI,$$

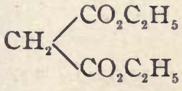


$$CH_3-\overset{Ocu}{CH}=CH-CO_2C_2H_5+CH_3COCl= \\ CH_3-\overset{O-COCH_3}{C}=CH-CO_2C_2H_5+cuCl.^{1}$$

(See Nef: Ann.,266, 103, 110, and 287, 270.)

With alkyl iodides, compounds containing the alkyl combined with carbon are almost exclusively formed.

This method has been of very great value in obtaining derivatives of acetoacetic ester, $CH_3COCH_2CO_2C_2H_5$, malonic ester,



$CH_2\begin{cases}CO_2C_2H_5\\CO_2C_2H_5\end{cases}$, and other compounds.

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[1] In this case "cu" is used to represent an *equivalent* instead of an atom of copper.

Acetoacetic acid and almost all other β-ketonic acids are extremely unstable in the free state. Hence, if the esters of these acids are saponified, decomposition products are usually obtained instead of the free acid. These products vary according to the nature of the ester and the means used for its saponification. In general, saponification with acids causes decomposition with loss of carbon dioxide and formation of a ketone (ketonic decomposition):

$$\underset{\text{Acetoacetic ester}}{CH_3COCH_2CO_2C_2H_5} + H_2SO_4 + H_2O =$$

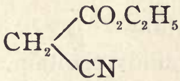
$$\underset{\text{Acetone}}{CH_3COCH_3} + C_2H_5OH + H_2SO_4 + CO_2.$$

(See also Baeyer: Ann., **278**, 90, for the saponification of succinylosuccinic ester.)

Saponification with strong bases, on the other hand, tends to favor the formation of acids (acid decomposition).

$$CH_3COCH_2CO_2C_2H_5 + 2KOH = CH_3CO_2K + CH_3CO_2K + C_2H_5OH.$$

Free malonic acid and its derivatives, that is, all compounds having two carboxyls combined with the same carbon atom, although stable at ordinary temperatures, are decomposed when heated to 150°-200°, and many of them, also, when heated with moderately strong, not concentrated, sulphuric acid. The value of acetoacetic ester for synthetic purposes is lessened because of the difficulty of securing a clean "acid decomposition" and, since the same product may usually be obtained by the use of malonic ester, the latter is now more frequently used in syntheses.

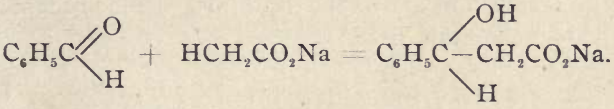
Cyanacetic ester,  $CH_2\begin{cases} CO_2C_2H_5 \\ CN \end{cases}$, may be condensed with alkyl halides by the same methods used for malonic ester and it sometimes gives normal products when malonic ester fails to do this. Thus it may be used to prepare trimethyl succinic acid from bromoisobutyric ester, $(CH_3)_2CBrCO_2C_2H_5$, while malonic ester gives methyl glutaric ester as the chief product. (Bone and Spranklin: J. Chem. Soc., **75**, 854; Noyes: Am. Chem. J., **33**, 358.)

In some cases the sodium compound of malonic ester may be prepared and used in a toluene solution to advantage and in others it is well to employ magnesium ethylate prepared by the use of magnesium amalgam in alcoholic solution. (Noyes and Kyriakides: J. Am. Chem. Soc., **32**, 1058.)

Another method of condensation used for the preparation of acids, known as Perkin's synthesis (Perkin: Ann. **147**, 230; Ber., 8, 1599; Jahresb., *1877*, 789; Tiemann, Herzfeld: Ber., **10**, 68), consists in heating a mixture of an aldehyde, a sodium salt, and acetic anhydride. One of the most common illustrations is the synthesis of cinnamic acid, which appears to take place as follows:

$$\underset{\text{Benzaldehyde}}{C_6H_5CH\boxed{O + H_2}}CHCO_2Na = \underset{\text{Sodium cinnamate}}{C_6H_5CH{=}CHCO_2Na} + H_2O.$$

The reaction has been shown to take place in two stages and consists, first, in an addition of the sodium salt to the aldehyde group:

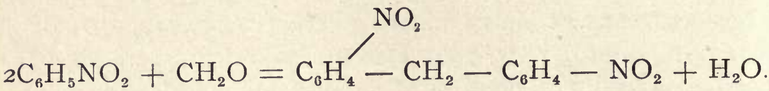


$$C_6H_5C\begin{matrix}{/\!\!/}O\\ \diagdown H\end{matrix} + HCH_2CO_2Na = C_6H_5C\begin{matrix}\diagup OH\\ -CH_2CO_2Na.\\ \diagdown H\end{matrix}$$

This addition is followed, under the influence of the acetic anhydride, by loss of water. The addition always takes place with the methyl, methylene or methin group adjacent to the carboxyl. Unlike the acetoacetic ester syntheses, the addition may take place with a methin group as well as with methyl and methylene groups, but in that case there can be no loss of water, and a hydroxy acid is formed. This is one of the most important proofs that the course of the reaction is as given. Historically this reaction was first used in the synthesis of cumarin by Perkin. Later, cinnamic acid and its derivatives became of especial interest because of their use by Baeyer in the synthesis of indigo.

Knoevenagel (Ber., **27**, 2345; Ann., **281**, 104) discovered a similar synthesis in which formaldehyde is used, and condensation takes place under the influence of some organic base. The mechanism of the reaction is not clearly understood.

Another similar condensation, but one which does not lead to the formation of an acid, is that of formaldehyde, with derivatives of benzene and its homologues, under the influence of concentrated sulphuric acid.

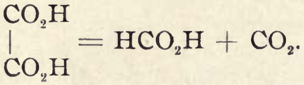


$$2C_6H_5NO_2 + CH_2O = C_6H_4\overset{NO_2}{\diagup} - CH_2 - C_6H_4 - NO_2 + H_2O.$$

(Schöpff: Ber., 27, 2321.)

IV. Decomposition of Bibasic Acids.—This method of preparation is used in connection with the synthesis by condensation of derivatives of malonic acid. In the case of acids where the two carboxyl groups are not combined with the same carbon atom, a clean decomposition cannot usually be effected by heat alone. In some cases, however, one of the carboxyls may be removed by heating the barium salt of a bibasic acid with sodium methylate (Mai: Ber., 22, 2136).

The decomposition of oxalic acid may be considered as a special case under this head:



$$\begin{matrix}CO_2H\\ |\\ CO_2H\end{matrix} = HCO_2H + CO_2.$$

The decomposition effected by heat alone is unsatisfactory in this case, also, and heating with glycerol is practically used. The glycerol appears to form an ester, $C_3H_5\Big\langle\begin{matrix}OCHO\\ (OH)_2\end{matrix}$, with the formic acid as it is formed. This ester then decomposes with the water present, yielding formic acid and regenerating the glycerol.

V. *Preparation from Natural Products.*—Many acids, as stearic, oleic, succinic, benzoic and others, occur in nature in the form of esters or glucosides, and may be obtained from these by saponification or decomposition by acids or alkalies.

$$\underset{\text{Stearin}}{(C_{17}H_{35}CO_2)_3.C_3H_5} + 3KOH = \underset{\text{Potassium stearate}}{3C_{17}H_{35}CO_2K} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}.$$

The preparation of acids by oxidation of other compounds has already been referred to. Many other illustrations of the preparation of acids from natural products might be given, but most of these are individual rather than general, and their discussion would be out of place here.

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45. Preparation of Acids by Decomposition of Bibasic Acids.—Formic acid, $H.CO_2H$. (Methanoic acid.)

Literature.—Berthelot: Ann. chim. phys. [3], **46**, 477; Ann., **98**, 139; Seekamp: *Ibid*, **122**, 113; Lorin: Ann. chim. phys., [4], **29**, 367; Romburgh: Compt. rend., **93**, 847; Roscoe: Ann., **125**, 320; Maquenne: Bull. soc. chim., [2], **50**, 662; Liebig: Ann., **17**, 69.

50 grams glycerol.
50 grams oxalic acid.

Place in a 150 cc. distilling bulb 50 grams of glycerol, and 50 grams of crystallized oxalic acid. Insert a thermometer, immersed in the liquid. Connect with a condenser, and heat with a low flame till the thermometer rises slowly to 105°. Allow to cool to about 50°, add 50 grams more of oxalic acid and distil again, always over a low flame and slowly till a temperature of 115° is shown by the thermometer. Repeat almost indefinitely, distilling to a temperature of 115°-125°. The acid coming over in the later distillations will be stronger than that of the first. The residue may be used for the preparation of allyl alcohol (see **21**, p. 69).

Pure formic acid cannot be obtained from the dilute acid by distillation, the tendency being for a dilute acid to become more concentrated, or a concentrated acid weaker by distillation, till an acid boiling at 107° and of 77 per cent. finally passes over. Weaker acids may be concentrated to this strength by distillation. A nearly anhydrous acid can then be obtained by dissolving anhydrous oxalic acid in this acid with the aid of heat, in such amount that on crystallizing with two molecules of water it will somewhat more than combine with all of the water present. After the oxalic acid has crystallized, the formic acid is poured off and distilled.

An anhydrous acid may also be obtained by the decomposition of the lead salt with hydrogen sulphide.

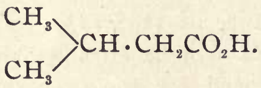
Formic acid melts at 8.3°, boils at 101°, and has a specific gravity of 1.2256 at 15°. The lead salt, which is easily prepared by dissolving lead carbonate in the hot dilute acid, is the most characteristic. It dissolves in 5½ parts of hot water, and in 63 parts of water at 16°. The copper salt also crystallizes well.

When heated with concentrated sulphuric acid, formic acid decomposes into water and carbon monoxide. On warming, it reduces solutions of silver salts with the separation of metallic silver. On warming with mercuric chloride calomel separates. On heating the sodium salt with caustic soda, hydrogen is liberated.

The specific gravity of the dilute acid is as follows:

Per cent. CH_2O_2	Specific gravity at 15°
10	1.025
30	1.080
50	1.124
70	1.161
100	1.223

46. Preparation of an Acid by Oxidation of an Alcohol.—Isovaleric acid (3-methylbutanoic acid).



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big\rangle CH\cdot CH_2CO_2H.$$

Literature.—Dumas u. Stas: Ann., 33, 156; 35, 143; Pierre and Puchot: Ann. chim. phys., [4], 29, 229; Stalmann: Ann., 147, 129; Erlenmeyer u. Hell: *Ibid*, 160, 275; Duclaux: Compt. rend., 105, 171.

100 cc. amyl alcohol (3-methyl butanol).
100 grams sodium pyrochromate.[1].
200 cc. water.
90 cc. concentrated sulphuric acid.
90 cc. water.

In a one liter flask place 100 cc. amyl alcohol (fusel oil), 100 grams of powdered sodium pyrochromate, and 200 cc. of water. Place in the mouth of the flask a stopper bearing a small, upright condenser having a rather wide tube. (Fig. 24, p. 68.) Add in small portions, through the condenser tube, a cooled mixture of 90 cc. of concentrated sulphuric acid and 90 cc. water. Shake vigorously and take care that the addition of the acid is so regulated that the reaction does not become too violent. The flask may be cooled occasionally by setting it in cold water, if necessary.

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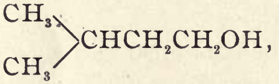
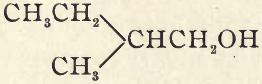
[1] The use of sodium rather than potassium pyrochromate is advised in this and other cases because of the greater solubility of the salt.

When the acid has all been added and the mixture no longer tends to grow warm when shaken, remove the condenser and replace it by a stopper bearing two glass tubes, one reaching nearly to the bottom of the flask, and the other a short bent tube leading to a condenser as shown in Fig. 23, p. 71. Distil by passing into the flask a rapid current of steam.

The oxidation converts a part of the amyl alcohol into valeric acid, which then combines with another part of the alcohol to form an ester.

The distillation should be continued as long as the ester continues to come over. Separate the ester from the aqueous solution, by means of a separatory funnel, saving both. Put the ester into a 500 cc. flask with 60 cc. of the aqueous solution and 30 grams of solid caustic soda. Adjust an upright condenser, as before, and boil gently for fifteen minutes, placing the flask on a thin asbestos board or on a wire gauze covered with a thin sheet of asbestos paper. Then add the remainder of the aqueous solution, which contains some valeric acid, and distil, either directly or with steam as long as amyl alcohol comes over. The amyl alcohol, which is recovered, may be saved for use in a new oxidation. Concentrate the residue in the distilling flask to about 100 cc. by evaporation in a porcelain dish. Transfer to a flask, cool, and add 50 cc. of dilute sulphuric acid (1:1 by volume). Separate the valeric acid by means of a separatory funnel, drawing off the solution below and pouring the acid out of the top of the funnel into a dry, 50 cc. flask. Add 5 grams of fused calcium chloride, stopper loosely and warm for ten minutes on a water-bath. Cool, pour off the acid into a small distilling bulb and distil, using a thermometer and an air condenser (See Fig. 11, p. 26.) Collect in dry test-tubes the fractions: below 168°, 168°-178° and 178°-190°. Clean the distilling bulb and put in the low boiling fraction and distil till the thermometer reaches 170°, add the second fraction and distil into the same receiver till the thermometer again reaches 170°, then into the second receiver. Establish two or three new fractions, according to the rate at which the thermometer rises as the acid comes over, the object being to obtain as large a fraction as possible within an interval of one or two degrees on each side of what appears to be the true boiling-point of the acid. (See p. 26 for further details and for corrections for the thermometer.) The fractional distillation should be repeated till a main fraction is obtained boiling, in this case, within an interval of one degree. Yield about 22 grams.

Since ordinary amyl alcohol, or fusel oil, consists chiefly of 3-methylbutanol,  $\begin{matrix} CH_3 \\ CH_3 \end{matrix} \rangle CHCH_2CH_2OH$, the valeric acid obtained from it will consist mainly of the acid corresponding to this formula. Fusel oil contains, however, 10 to 20 per cent. of what is supposed to be a partially racemic mixture of the 2-methyl butanols,  $\begin{matrix} CH_3CH_2 \\ CH_3 \end{matrix} \rangle CHCH_2OH$, and these will, of course, give the corresponding acids by oxidation. Hence, the valeric acid prepared from fusel oil, is probably a mixture of at least two or three chemical individuals. The perfectly pure isovaleric acid (3-methyl butanoic acid) can be obtained by conversion of the acid into the barium salt, crystallizing the latter from water and then separating the acid from the pure salt.

Pure isovaleric acid is a colorless liquid with an unpleasant odor. It boils at 176.3° and has a specific gravity of 0.931 at 20°. It dissolves in 23.6 parts of water at 20°, but the addition of soluble salts causes most of it to separate from the solution. The chromic acid mixture oxidizes it to acetic acid and carbon dioxide.

The barium salt crystallizes in small prisms or thin leaflets. The silver salt crystallizes in leaflets soluble in 400 parts of water at 20°, or in 204 parts of water at 80°. The salts, when thrown on water, rotate rapidly. This is characteristic of the salts of many of the higher fatty acids.

The most serious objection to this preparation is the very unpleasant odor accompanying it. The operations should be conducted under a hood as far as possible, and care should be taken to avoid contact of the valeric acid with the hands or clothing.

47. Oxidation of a Ketone.—Separation of Two Fatty Acids. —Propionic and butyric acids, $C_2H_5CO_2H$ and $C_3H_7CO_2H$ (propanoic and butanoic acids).

Literature.—Papow: Ann., 145, 283; 161, 291; Liebig: *Ibid*, 71, 355; Fitz: Ber., 11, 46; Hecht: Ann., 209, 319; Erlenmeyer u. Hill: *Ibid*, 160, 296; Baeyer: *Ibid*, 278, 101.

10 grams normal butyric acid (butanoic acid).
25 grams quicklime.

6 grams dipropylketone (4 heptanone).
25 grams potassium pyrochromate.
120 cc. water.
20 cc. concentrated sulphuric acid.

Weigh in a small porcelain dish 10 grams of normal butyric acid. Add carefully, taking care that the mixture does not become so hot as to volatilize any appreciable amount of the acid, 25 grams of powdered quicklime. Mix thoroughly and powder in a mortar. Place the mixture in a 50 cc. flask, clamp the latter in a horizontal position, and connect it by means of perforated cork stoppers and a bent glass tube with a small condenser. Distil by heating carefully with a free flame. Collect the distillate in a small flask, add a little dry potassium carbonate to remove a small amount of acid and water which are present, weigh, pour off into a 500 cc. flask and weigh again to determine the amount of crude ketone formed. For six grams of the ketone add a cooled mixture of 25 grams potassium pyrochromate, 20 cc. concentrated sulphuric acid and 120 cc. of water, using more or less, according to the amount of the ketone. Boil for three hours on a thin asbestos plate, with a reversed condenser (Fig. 24, p. 68). Transfer the mixture to a 200 cc. distilling bulb and distil in a current of steam (Fig. 25, p. 54), collecting the distillate in successive portions of 10, 25, 50, and 100 cc. Prepare, separately, calcium salts of the acid in the first and last portions by boiling for a short time with a small quantity of pure calcium carbonate, and filtering. Concentrate each solution to 10 cc. or less, and add 5 cc. of a ten per cent. solution of silver nitrate. Filter off the silver salt, best on a small Witt plate (Fig. 29), wash, dry, and determine the per cent. of silver in each salt by careful ignition in a porcelain crucible.

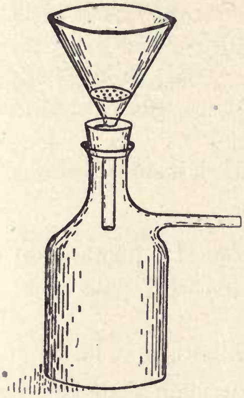


Fig. 29.

The oxidation gives, in this case, a mixture of propionic and butyric acids. On distilling the mixture in a current of steam the butyric acid, which is less soluble and which also has the lower ionization constant,[1] comes over mainly in the first portion, while the propionic acid comes over afterwards. A single distillation as directed will usually, when but two acids are present, give a sufficient separation so that the analyses of the silver salts leave no question as to the composition of the acids.

Butyric acid boils at 162°, and has a specific gravity of 0.978 at 0°. Propionic acid boils at 141°, and has a specific gravity of 1.013 at 0°.

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[1] The ionization constants should be found in Beilstein's Handbuch.

100 parts of water dissolve 0.48 parts of normal silver butyrate and 0.836 parts of silver propionate at 20°.

48. Preparation of an Acid from a Natural Product.—Stearic acid, $C_{17}H_{33}CO_2H$.

Literature.—Pebal: Ann., 91, 138; Heintz: Ann., 92, 290; Carnelly, Williams: Ber., 12, 1360; J. Chem. Soc., 35, 563; Krafft: Ber., 15, 1724; 16, 1722; Saunders: Jahresb., *1880*, 831; David: Z. anal. Chem., 18, 622; Krafft: Ber., 22, 819; Hehner and Mitchell: J. Am. Chem. Soc., 19, 32.

100 cc. alcohol.
100 grams tallow.

35 grams potassium hydroxide.
35 cc. water.

90 cc. hydrochloric acid (sp. gr. 1.1).
Magnesium acetate.

Melt 100 grams of tallow and pour it into a 500 cc. flask, add 100 cc. of alcohol and warm on a water-bath. Add in small portions 35 grams of caustic potash dissolved in 35 cc. of water. After all has been added, dilute with 200 cc. of cold water. Add 90 cc. of hydrochloric acid (4 cc. = 1 gram), and warm till the fatty acids melt and collect on top. Cool and separate the acids from the solution. Dissolve the acids in 500 cc. of warm alcohol, cool somewhat, and add enough of a solution of magnesium acetate[1] to precipitate 20 grams of stearic acid. Stir for five minutes, filter on a plate, and wash once with strong alcohol. To the filtrate add the same amount of the acetate, filter on a new filter, and repeat as often as a precipitate is obtained. From the last filtrate an impure oleic acid can be precipitated by water.

Decompose each of the magnesium precipitates separately by warming and stirring with dilute hydrochloric acid till the fatty acid separates and melts to a clear liquid, and then allow each to cool and solidify. Crystallize each portion of the acids obtained from 15-20 times its weight of strong alcohol. Determine the melting-points of each set of crystals obtained, unite portions having nearly the same melting-point and crystallize again, and repeat till a considerable quantity of pure stearic acid is obtained. It will usually be found best to crystallize rather slowly by spontaneous cooling, and not to allow the temperature to fall too low. It is also wise to separate the crystals from the mother liquors soon after they form, as the mother liquors, in fractional crystallization will often form supersaturated solutions of the substance which is to be removed.

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[1] Prepare the solution by dissolving 16.8 grams of magnesium carbonate or 8 grams of freshly ignited magnesium oxide in 85 cc. of acetic acid (30 per cent.), filtering, and washing to a volume of 100 cc. One cc. of the solution will precipitate 1.136 grams stearic acid.

The impure oleic acid referred to above may, if desired, be converted into the lead salt by digesting with litharge on the water-bath, and the lead oleate separated from the lead salts of other acids by solution in ether, or in alcohol (of sp. gr. 0.82) at 65°. The oleic acid is set free by digesting the salt with hydrochloric acid, the acid converted into the barium salt, and the latter crystallized from alcohol. (Gottlieb: Ann., **57**, 38.)

Distillation under diminished pressure may also be used with advantage in purifying the fatty acids. The boiling-points and melting-points are as follows:

BOILING-POINTS

	Palmitic	Stearic	Oleic
At 15 mm............	215°	232°	232.5°
At 100 mm............	271.8°	291°	286°
At 760 mm............	339°-356°	359°-383°	..

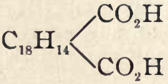
MELTING-POINTS

Palmitic	Stearic	Oleic
62°	69.2° or 71°-71.5°	14°

Stearic acid crystallizes from alcohol in leaflets. It is soluble in 40 parts of cold absolute alcohol, in its own weight of alcohol at 50°.

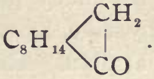
Palmitic acid dissolves in 10 parts of cold alcohol. 100 cc. of alcohol of sp. gr. 0.8183 will dissolve at 0° about 0.15 gram of stearic acid and about 1.2 gram of palmitic acid. (Hehner and Mitchell.)

49. **Oxidation of a Cyclic Ketone.**—Camphoric acid,



$$C_{18}H_{14}\begin{cases}CO_2H\\CO_2H\end{cases}.$$

Literature.—Kosegarten: Dissertation, Göttingen, 1785; Laurent: Ann., 22, 135; Wreden: *Ibid,* 163, 323; Maissen: Ber., 13, 1873; Helle: Dissertation, Bonn, 1893; Noyes: Am. Chem. J., 16, 501; Aschan: Structur und Stereochemische Studien in der Campher Gruppe, Helsingfors, 1895. Structure of Camphor, Komppa: Ann., 370, 209.

50 grams camphor, 

$$C_8H_{14}\left\langle\begin{array}{l}CH_2\\ |\\ CO\end{array}\right. .$$

300 cc. nitric acid (sp. gr. 1.42).
200 cc. water.

Place in a one liter flask 50 grams of camphor, 200 cc. of water and 300 cc. of nitric acid (sp. gr. 1.42). Close the mouth of the flask with a tube of the form shown in the cut, filled with water. The tube is easily made by taking a tube 40 cm. long, which will pass easily into the neck of the flask, sealing it at one end, and blowing a small bulb at about 10 cm. from the sealed end.

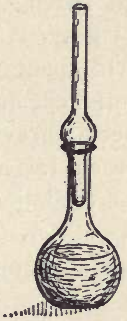
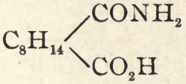
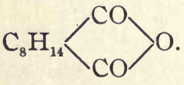
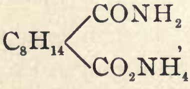
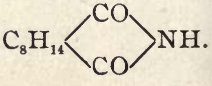


Fig. 30.

Heat the mixture on a boiling water-bath or a steam-bath for seventy two hours. Cool, filter off the camphoric acid with the pump on a Hirsch funnel or a Witt's plate, (Fig. 29, p. 120) using an "S. & S." hardened filter. After sucking away the mother-liquors, stop the pump, add enough water to barely cover the acid, and suck off again. In all cases where the substance to be washed is appreciably soluble this method should be employed, as bodies may, in this way, be effectively washed by the use of a much smaller quantity of the solvent than if the pump is allowed to act while the solvent is poured over the precipitate. By washing three or four times in this manner the nitric acid will be almost completely removed, and the camphoric acid, after drying, will be sufficiently pure for many purposes, and especially for the preparation of the anhydride, as the latter is easily purified by crystallization from alcohol. The acid will, however, contain some unchanged camphor and, probably, a small amount of camphoramidic acid,  $C_8H_{14}\Big\langle\begin{matrix}CONH_2\\CO_2H\end{matrix}$. If a pure acid is desired, after washing once, transfer the acid to a beaker, add 150 cc. of water and 60-65 cc. of ammonia (0.96), enough to convert the acid into the ammonium salt. Filter the cold solution, and add it slowly, with constant stirring, to 70 cc. of hydrochloric acid (sp. gr. 1.11, 4 cc. = 1 gram HCl). Filter on a plate and wash with cold water. Yield about 30 grams of pure acid.

The acid mother-liquors, if kept separate from the washings, may be brought up to a specific gravity of 1.29 by the addition of strong nitric acid and used for a second, and the mother-liquors of that, for a third oxidation. The yield in the later oxidations will be somewhat greater. The filtrate from the third oxidation will contain considerable amounts of camphoronic acid, $C_6H_{11}(CO_2H)_3$.

Camphoric acid crystallizes in leaflets or prisms which melt at 187°. In a ten per cent. alcoholic solution it shows a rotation of polarized light $[\alpha]_j = +49\ 7°$, or $[\alpha]_D = +47.8°$. 100 parts of water, dissolve 0.625 parts of the acid at 12°, and 8 to 10 parts at 100°. On heating alone, or with acetyl chloride, or acetic anhydride, it is converted into the anhydride,  $C_8H_{14}\Big\langle\begin{matrix}CO\\CO\end{matrix}\Big\rangle O$. The latter is converted by ammonia into the ammonium salts of α-camphoramidic and β-camphoramidic acids,  $C_8H_{14}\Big\langle\begin{matrix}CONH_2\\CO_2NH_4\end{matrix}$, which on heating give an imide,  $C_8H_{14}\Big\langle\begin{matrix}CO\\CO\end{matrix}\Big\rangle NH$.

The ammonium salt of the α-camphoramidic acid is less soluble than that of the β-acid while sodium salt of the β-camphoramidic acid is less soluble than that of the α-acid. A separation of the two acids can be easily effected on the basis of these facts and of the further fact that both acids are nearly insoluble in water.

50. Oxidation of a Homologue of Benzene with a Halogen Atom in the Side Chain.—Benzoic acid, $C_6H_5CO_2H$.

Literature.—Grimaux, Hauth: Bull. soc. chim., 7, 100; Lunge: Ber., 10, 1275; Carius: Ann., 148, 51 and 59; Wagner: Jahresb., 1880, 1289; V. Meyer: Ber., 24, 4251; Sandmeyer: *Ibid*, 17, 2653.

20 grams benzyl chloride.
46 grams nitric acid (sp. gr. 1.42).
55 grams water.

Put into a 300 cc. flask with a narrow neck, from which the lip has been cut off, so as to leave the neck straight to the top, 20 grams of benzyl chloride, 46 grams (32 cc.) of concentrated nitric acid, and 55 cc. of water. Slip over the neck of the flask a short piece of rubber tubing, and pass through this the tube of an upright condenser of such size as to just pass easily into the neck of the flask. By this means a tight joint is formed, and at the same time the vapors scarcely come in contact with the rubber. Place the flask on a wire gauze and boil gently for 2-3 hours, or until the oxides of nitrogen nearly disappear within the flask, and the benzoic acid formed largely sinks to the bottom of the liquid. There is some tendency for the liquid to boil explosively, but there is less trouble from this source if a round-bottomed flask is used and this is heated directly over a small flame which is brought close to the wire gauze, than if the flask is heated on a sand bath or on an asbestos paper. A boiling capillary, (Scudder: J. Am. Chem. Soc., 25, 163) or a few small pieces of porous porcelain may also be used to advantage.

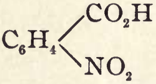
Cool, filter on a plate, suck off the mother-liquors, stop the pump, moisten thoroughly with water and suck off again. Dissolve the benzoic acid in 70 to 80 cc. of sodium hydroxide (10 per cent.), added to alkaline reaction, filter on a plain moist filter, or pour off from any benzyl chloride which remains undissolved, put the solution in a flask or large beaker and pass through it a rapid current of steam till the vapors no longer smell of benzyl chloride. Precipitate the benzoic acid again by adding 18 to 20 cc. of concentrated hydrochloric acid. Cool thoroughly, filter on a plate, and wash once. Crystallize from a mixture of 30 cc. of alcohol with 10 to 15 cc. of water.

The benzoic acid prepared in this way retains a little chlorobenzoic acid from which it appears to be nearly or quite impossible to free it. This can be detected by heating a little of the acid, mixed with sodium carbonate, on platinum foil till it chars, adding a little potassium nitrate and heating again till white, dissolving the residue in water and adding dilute nitric acid, and silver nitrate. Yield 13 to 15 grams.

Benzoic acid cvrystallizes in needles or leaflets which melt at 121.4°. It boils at 249°. 100 parts water dissolve 0.27 part of the acid at 18°, and 2.19 parts at 75°. An impure acid is more easily soluble. It is soluble in about 3 parts of strong alcohol at 15°. It is easily volatile with water vapor. The vapors of the acid produce a coughing sensation.

51. Oxidation of the Side Chain of a Hydrocarbon Derivative.

—Ortho- and para-nitrobenzoic acids,



$C_6H_4 \begin{cases} CO_2H \\ NO_2 \end{cases}$.

Literature.—Beilstein: Ann., **133**, 41; **137**, 302; Hofmann: *Ibid,* **97**, 207; Weith: Ber., **7**, 1057; Monnet, Reverdin, Nölting: *Ibid,* **12**, 443; Nölting, Witt: *Ibid,* **18**, 1336.

40 grams toluene.
50 cc. sulphuric acid (1.84).
30 cc. nitric acid (1.42).

Place in a 300 cc. flask, 40 grams (46 cc.) of toluene and add in small portions a cooled mixture of 50 cc. of concentrated sulphuric acid, and 30 cc. of nitric acid (1.42). Shake vigorously and cool after each addition, taking care that the temperature does not rise above 30°. After the acid has all been added, shake vigorously for ten minutes, keeping the temperature down as before. Pour into about 700 cc. of water. The nitrotoluene will now sink to the bottom. Separate from the acid liquid with a separatory funnel, and wash by shaking the nitrotoluene again with about 100 cc. water. In this and all similar cases where a heavy liquid is to be separated from water, it is best to use a flask or separatory funnel of such size that the mixture will fill it nearly to the top, as otherwise a considerable amount of the heavy liquid may remain floating on top of the water. Separate the nitrotoluene as completely as possible from the water, put it in a small flask, add 10 grams of fused, granulated calcium chloride, and warm in a water-bath with the flask covered with a watch-glass for half an hour, or allow it to stand over night. Pour the nitrotoluene off into a distilling bulb. Distil, using a glass tube as a condenser (see Fig. 11, p. 26). The portion distilling below 200° consists principally of unchanged toluene, and may be saved. That distilling between 200°-240° consists chiefly of ortho- and paranitrotoluene, while that boiling above 250° consists chiefly of dinitrotoluene. Ortho-nitrotoluene boils at 220° and melts at — 10.5°. Paranitrotoluene boils at 239° and melts at 54°. The two can be partially separated by fractional distillation, and the para compound can be obtained pure by crystallization from alcohol. For the remainder of this preparation the mixture boiling from 200°-240° may be used.

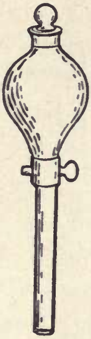


Fig. 31.

15 grams mixed nitrotoluenes.
100 cc. water.
10 cc. sodium hydroxide (10 per cent.).
35 grams potassium permanganate.
350 cc. water.

Arrange a one liter flask with an upright condenser, a bent thistle tube, and a bent tube to convey steam to the bottom of the flask, as indicated in the figure. (See Fig. 32.)

Place in the flask 15 grams of the mixed nitrotoluenes, 100 cc. of water, and 10 cc. of a 10 per cent. solution of sodium hydroxide. Add about 50 cc. of a warm 10 per cent. solution of potassium permanganate. Pass in a current of steam rapidly till the solution boils, and then just fast enough to keep the contents of the flask agitated, and so that a small amount of steam condenses above. Add more of the permanganate solution at frequent intervals till 35 grams of the salt in all have been added. Continue the current of steam until the pink color of the permanganate disappears, or till the drops of nitrotoluene cease to appear in the condenser. If unreduced permanganate is still present, add a few drops of alcohol, and shake to reduce it. Filter hot, from the oxides of manganese, on a filter plate or Hirsch funnel, and wash twice with water. Concentrate the filtrate to about 40 cc., and precipitate the mixed ortho- and

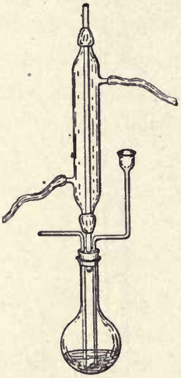


Fig. 32.

paranitrobenzoic acids with 25 cc. of concentrated hydrochloric acid. Cool very thoroughly, filter on a plate, and wash twice with a very small amount of cold water, sucking off the mother-liquors thoroughly each time (see 47, p. 120). Convert into the barium salts by boiling with about 12 grams of barium carbonate and 200 cc. of water. Filter hot and cool the filtrate. A considerable portion of the barium salt of the para acid will separate. Filter, wash once with cold water and concentrate the filtrate and washings to a very small volume. Cool quickly and filter at once on a plate. Moisten the residue several times with a small amount of cold water and suck off. Concentrate the filtrate and washings, and crystallize the ortho salt by allowing the cold, concentrated solution to stand for some time. Recrystallize both the ortho and para salts from hot water, saving the mother-liquors and working them up in such a manner as to secure as large an amount as possible of each salt in a pure condition.

The separation of two substances by crystallization is a problem which often presents itself in organic chemistry, and it frequently requires very careful work and good judgment to secure both substances in pure condition without serious loss of material. As the substance which is present in least amount, or which is most easily soluble, is liable to form supersaturated solutions, it is usually advisable to filter off a substance which has crystallized as soon as its separation from the solution appears to be practically complete. The separation can frequently be hastened by vigorous stirring, and by the addition of a fragment of the pure substance, when crystals are slow in starting. Occasionally, however, a substance may form crystals sufficiently large to be separated mechanically from others with which they are mixed. In such cases the crystallizations must be allowed to proceed slowly and undisturbed, and it may be well to allow the solution to evaporate slowly at ordinary temperatures, or *in vacuo* over sulphuric acid. Large crystals of the barium salt of orthonitrobenzoic acid may be obtained in this way.

Crusts which separate on the walls of a dish or beaker during evaporation, usually consist of a mixture, and should be brought back into the solution and redissolved by heating before the latter is cooled for crystallization. The formation of such crusts can best be avoided by allowing solutions in volatile solvents, as benzene or alcohol, to stand during crystallization in tightly closed flasks. Wide mouthed Erlenmeyer or Soxhlet flasks are very useful for this purpose.

In using a solvent, a very common mistake is to use too large an amount. A small amount should always be added at first, unless the properties of the substance are familiar, and then more, if the substance cannot be brought into solution.

With substances which separate very easily on cooling the solution, the opposite mistake may be made, if the solution requires filtration. In such cases, the substance should be taken only in such amount as will dissolve very easily in the amount of the solvent used, and care must be taken to prevent the crystallization of the substance on the filter, either by the use of a plate, (not a Hirsch funnel), and pouring only as fast as the solution runs through the filter, or by the use of a hot water funnel. The latter is rarely necessary, if the chemist has acquired the necessary experience, except in cases where a precipitate clogs the filter badly.

When alcohol is used as a solvent, the yield of crystals may, sometimes, be increased by adding some water to the solution before it cools. When the impurities are soluble in dilute alcohol, this may be used with advantage instead of pure alcohol to wash the crystals.

It should be remembered that strong alcohol is not a suitable solvent for some acids and some nitro-phenols because of the ease with which they form esters.

Crystallization is the most valuable means in the hands of the chemist for obtaining pure substances. When it can be applied, it almost always gives purer substances than fractional distillation. In working with new substances, success often depends largely on the choice and use of proper solvents, and it is a matter to which the beginner should give very careful attention.

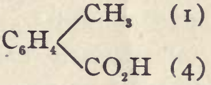
In working with new compounds valuable hints can almost always be obtained by learning from text-books or chemical journals the conduct of closely related substances which have been previously known.

Orthonitrobenzoic acid crystallizes in colorless triclinic prisms, which have a sweet taste, melt at 147°, and dissolve in 164 parts of water at 16.5°.

Paranitrobenzoic acid crystallizes in yellow leaflets, which melt at 240°, and dissolve in 1200 parts of water at 17°, or in 140 parts at 100°.

The *barium salt* of the *ortho* acid crystallizes with 3 molecules of water, in yellow, triclinic crystals, which are easily soluble in water.

The *barium salt* of the *para acid* crystallizes with 5 molecules of water, in yellow, monoclinic prisms, soluble in 250 parts of cold, and 8 parts of hot water.

52. Preparation of an Acid from an Amine through a Diazonium Compound.—Paratoluic acid,  $C_6H_4\begin{cases} CH_3 & (1) \\ CO_2H & (4) \end{cases}$.

Literature.—Spica and Paterno: Ber., 8, 441; Sandmeyer: *Ibid,* 17, 1633, 2653; 18, 1492; Baeyer and Tutein: *Ibid,* 22, 2178; Herb: Ann., 258, 8.

21.4 grams paratoluidine.
39 grams concentrated hydrochloric acid.
150 cc. water.
50 grams ice.

14 grams sodium nitrate.
70 cc. water.

55 grams potassium cyanide.
100 cc. water.

50 grams copper sulphate.
100 cc. water.

10 grams tolunitrile.
30 cc. concentrated sulphuric acid.
20 cc. water.

In a one liter flask dissolve 50 grams of copper sulphate in 100 cc. of hot water. When the diazonium solution, given below, has been prepared, pour into the solution of copper sulphate, slowly, while the latter is heated to gentle boiling, in a hood with a good draught, 55 grams of potassium cyanide dissolved in 100 cc. of water. This converts the copper into cuprous cyanide with evolution of cyanogen. If the cuprous cyanide solution turns dark very rapidly, azulmic acid is formed by the decomposition of cyanogen held in solution. The presence of any appreciable quantity of this azulmic acid acts very unfavorably on the formation of the nitrile later. By boiling the copper sulphate solution gently during the addition of the potassium cyanide solution and by continuing the boiling for a few minutes at the end to expel the cyanogen a perfectly clear, slightly colored solution of cuprous cyanide will be obtained.

Put into a 400 cc. beaker 21 grams of paratoluidine, add 150 cc. of water, and 39 grams (33 cc.) of concentrated hydrochloric acid (sp. gr. 1.19). Add 50 grams of ice, and when the temperature has fallen nearly to 0°, add, in small portions, with stirring a solution of 14 grams of sodium nitrite in 70 cc. of water. For a discussion of the best condition for Sandmeyer's reaction see 92, p. 202.

After five or ten minutes, having meanwhile, completed the preparation of the cuprous cyanide solution, place in the mouth of the flask containing it a funnel, and pour in the diazonium solution, shaking the flask and keeping it hot on a boiling water-bath, taking care also that the solution does not froth over. As soon as all of the solution has been added, distil off the nitrile in a rapid current of steam (see Fig. 25, p. 71). If the distillation is sufficiently rapid, the nitrile will come over with 300 to 400 cc. of water. Cool the distillate in ice-water or a freezing mixture, till the nitrile solidifies, and separate the latter by quick filtration on a plate, or an a funnel loosely stoppered with cotton-wool. Care must be taken to transfer the nitrile to a dish or a bottle before it melts. If thought better, the nitrile can be brought to the surface by adding salt to the water, or it may be collected with a little ether, and separated with a separatory funnel. Yield about 15 grams.

Tolunitrile melts at 28.5° and boils at 218°.

For 10 grams of tolunitrile take a mixture of 30 cc. of concentrated sulphuric acid with 20 cc. of water. Boil in a small round-bottomed flask on an asbestos plate with an upright condenser till crystals of toluic acid appear in the latter. Cool, dilute, filter. Put the acid in a flask, dissolve in a little alcohol, and add hot water till the solution becomes turbid. Add 2 or 3 grams of animal charcoal, boil a short time, filter hot, and allow the acid to crystallize. Yield 8 to 9 grams from 10 grams of the nitrile.

Toluic acid crystallizes in white needles, which melt at 177°. It is very easily soluble in alcohol and ether, and easily soluble in hot water. It volatilizes readily with water vapor. In alkaline solution it is easily oxidized to terephthalic acid by potassium permanganate.

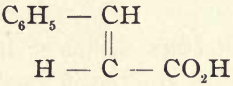
53. Condensation of an Aldehyde with the Sodium Salt of an Acid. Perkin's Synthesis.—Cinnamic acid,

$$C_6H_5 - CH = CHCO_2H.$$

Literature.—Perkin: Jsb. d. chem., *1877*, 789; J. Chem. Soc., **31**, 388; Tiemann, Herzfeld: Ber., **10**, 68; Edeleano, Budistheano: Bull. soc. chim. [3], **3**, 191; Michael: Am. Chem. J., **5**, 205. Also see preparation, **39**.

20 grams benzaldehyde.
30 grams acetic anhydride.
10 grams sodium acetate.

In a 100 cc. flask place 10 grams of recently fused and powdered, dry, sodium acetate, 30 grams acetic anhydride, and 30 grams benzaldehyde, both recently distilled. Connect with an upright air condenser tube, 1 cm. in diameter and 60-80 cm. long. Heat in a small paraffin bath to the boiling-point of the mixture, about 180°, for eight hours. Pour the contents of the flask while hot into a 500 cc. flask or distilling bulb. Rinse out with hot water and then distil with water vapor as long as benzaldehyde comes over. Add more water, if necessary, to dissolve the cinnamic acid, and a little bone-black. Boil and filter hot on a plain or plaited filter, previously moistened. To the filtrate add 13 cc. of concentrated hydrochloric acid. (Why is this desirable according to the theory of ionization?) The cinnamic acid will crystallize from the filtrate on cooling. If it does not have the proper melting-point, recrystallize from hot water.

Cinnamic acid crystallizes from water in colorless needles or leaflets, which melt at 133°. It dissolves in 3500 parts of water at 17°, much more easily in hot water. It combines with bromine to form a dibromide, $C_6H_5CHBr.CHBrCO_2H$, which on treatment with alcoholic potash gives phenyl propiolic acid, $C_6H_5C \equiv C - CO_2H$. Ordinary cinnamic acid appears to be the cistrans modification,  $\begin{array}{l} C_6H_5 - CH \\ \quad\quad\quad \| \\ H - C - CO_2H \end{array}$. Three other forms, one called isocinnamic acid, which melts at 58°, one called allocinnamic acid, which melts at 68°, and a fourth isocinnamic acid, which melts at 42°, are known. Since the accepted theory of stereoisomerism will account for only two isomers or stereomers, the existence of these forms has led to a very careful investigation of these acids. Liebermann: Ber., **23**, 141, 2511; **24**, 1102; **25**, 950; **26**, 1572; **27**, 2038; Fock: *Ibid,* **23**, 147, 2511; Ostwald: *Ibid,* **23**, 516; **24**, 1106; Stohmann: Z. physik. Chem., **10**, 418; Michael: Ber., **34**, 3640; Erlenmeyer, Jun.: Ber., **38**, 3499; **39**, 285; Erlenmeyer and Barkow: Ber., **39**, 1570; Biilmann: Ber., **42**, 182; **43**, 568; Riiber and Goldschmidt: Ber., **43**, 453; Liebermann, Ber., **42**, 1027.

A final conclusion has not, perhaps, been reached but the present tendency is to explain the extra forms on the basis of polymorphism.

For a quite different method of preparing cinnamic acid see 39, p. 99.

54. **Reduction of an Unsaturated Acid by Sodium Amalgam.**—Hydrocinnamic acid, $C_6H_5CH_2CH_2CO_2H$, (Phen-3-propanoic acid).

Literature.—Alexejew, Erlenmeyer: Ann., **121**, 375; **137**, 327; Gabriel, Zimmermann: Ber., **13**, 1680; Fittig, Kiesow: Ann., **156**, 249; Sesemann: Ber., **6**, 1086; **10**, 758; Conrad, Hodgkinson: Ann., **193**, 300; Conrad:

Ibid, 204, 174; Conrad, Bischoff: *Ibid,* 204, 180; Fittig, Christ: *Ibid,* 268, 122. For benzyl acetone, Ehrlich: *Ibid,* 187, 11; Jackson: Ber., 14, 890; Harries, Eschenbach: *Ibid,* 29, 383.

10 grams cinnamic acid.
60 cc. water.
27 cc. sodium hydroxide (10 per cent.).
135 grams sodium amalgam (3 per cent.).

Put in a 200 cc. wide-mouthed bottle 10 grams of cinnamic acid, 60 cc. of water, 27 cc. sodium hydroxide (10 per cent.), and 135 grams sodium amalgam (3 per cent.).[1] Shake for some time till the amalgam becomes liquid. Take out a few drops of the solution, dilute, pass carbon dioxide through it, or add a few drops of hydrochloric acid, a little sodium carbonate and then a drop of a very dilute solution of potassium permanganate. If the permanganate is decolorized or turns brown at once, cinnamic acid is still present and the solution must be warmed in a water-bath, shaken occasionally, and, if necessary, more amalgam added till the solution no longer decolorizes permanganate. This permanganate test has proved of great value for the detection of unsaturated compounds in many similar cases. The test cannot be applied to the alkaline solution without passing carbon dioxide through it, because it is masked by the formation of a green manganate.

When the reduction is complete, pour off from the mercury and precipitate the hydrocinnamic acid by adding 22 to 25 cc. of concentrated hydrochloric acid. The acid usually separates as an oil which solidifies on allowing the cold solution to stand. Filter off, and recrystallize from hot water. Yield 9 grams.

Hydrocinnamic acid crystallizes in long colorless needles which melt at 49°. It boils at 280°. It is easily soluble in boiling water, in alcohol, and in ether. It is volatile with water vapor, and solutions of it cannot be concentrated by boiling without loss. It is soluble in 168 parts of water at 20°.

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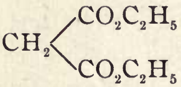
[1] Weigh out in a dry mortar 130 grams of pure mercury (amalgam from impure mercury is much less effective; Aschan: Ber. 24, 1865; E. Fischer: *Ibid.* 25, 1255). Clean 4 grams of sodium, cut off a thin slice and press it to the bottom of the mortar with the pestle, and press gently till the somewhat violent reaction takes place. Add a second piece in the same way and continue as rapidly as possible till all is added. If the operation is conducted quickly, all can be added before the mass solidifies. Break up the amalgam at once and transfer it to a tightly stoppered bottle.

The reduction of an unsaturated acid by sodium amalgam can only be carried out, apparently, when the double union is adjacent to the carboxyl. When the double union is further removed the reduction may often be carried out by first adding hydriodic acid and then reducing with zinc dust or the zinc-copper couple in an alcoholic solution and in presence of a little dilute acid. See **6**, p. 42, also Noyes and Blanchard: Am. Chem. J., 26, 288.

The reduction may also be effected electrolytically (Elbs: Uebungsbsp. elektrolyt. Darst. chem. Präparate; see also Bredt: Ann., **266**, 13); by ethyl or amyl alcohol and sodium, (Ladenburg, Baeyer). See Einhorn: Ann., **286**, 257; **295**, 173; Diels, Rhodius: Ber., **42**, 1072; by hydrogen in the presence of colloidal platinum or palladium, Paal and Gerum: Ber., **41**, 2273. For other methods of reduction see Meyer: Analyse u. Konstitutionsermittelung org. Verbindungen, looking up "Reduktion" in the index.

55. **Preparation of an Ester of a Bibasic Acid from a Halogen Derivative of an Acid.**—Malonic ester,  $CH_2<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$.

Literature.—Dessaignes: Ann., **107**, 251; Kolbe and Müller: *Ibid*, **131**, 348, 350; Finckelstein: *Ibid*, **133**, 338, 350; Conrad: *Ibid*, **204**, 134; Claisen and Venable: *Ibid*, **218**, 131; Kolbe and Müller: J. Chem. Soc., **17**, 109, (1864); Noyes: J. Am. Chem. Soc., **18**, 1105 (1896); Presence of cyanacetic ester in malonic ester, Noyes: J. Am. Chem. Soc., **23**, 397; Preparation of cyanacetic ester, *Ibid*, **26**, 1545.

50 grams monochloracetic acid.
45 grams acid sodium carbonate.
100 cc. water.

40 grams potassium cyanide.

100 cc. alcohol.
80 cc. concentrated sulphuric acid.

Put 50 grams of monochloracetic acid into a porcelain dish

20 cm. in diameter. Add 100 cc. of water, and 45 grams of acid sodium carbonate. Warm, stirring with a thermometer, till a temperature of 50°-60° is reached, and the effervescence has ceased. Place the dish on a sheet of asbestos paper on a tripod, in a hood with a good draught. Add 40 grams of powdered potassium cyanide, and stir vigorously with the thermometer. Warm only very gently till the reaction, which takes place with considerable evolution of heat and spontaneous boiling of the solution, is complete. Then raise the flame and evaporate rapidly, stirring constantly with the thermometer till a temperature of 130° is reached. During this part of the operation keep the window glass of the hood between the dish and the face, and cover the hand with a towel or glove to protect it from the particles of the mixture which are thrown out. Remove the dish from the flame, and continue to stir till the mass is cold. Transfer at once to a 500 cc. flask as the mass is very hygroscopic. Connect the flask with an upright condenser (see **20**, p. 68). Add 20 cc. of alcohol and then, in small portions, through the condenser, a cooled mixture of 80 cc. of alcohol with 80 cc. of concentrated sulphuric acid. After each addition, mix the contents of the flask as thoroughly as possible by shaking. When all of the mixture has been added, shake till the whole is thoroughly mixed, and then heat on the water-bath for an hour. Cool, add 150 cc. of cold water, and shake thoroughly. Filter on a Hirsch funnel or plate, and suck the liquid through as completely as possible. Stop the pump, moisten the salt with ether; after a minute or so draw this through, and repeat twice. Transfer the contents of the filtering flask to a separatory funnel and draw off the salt solution below. Add a small amount of a strong solution of sodium carbonate to the ethereal solution, and shake carefully with the funnel open at the top to allow the carbon dioxide to escape. When enough of the solution has been added to neutralize the free acid, insert the stopper and shake more vigorously, holding the stopper firmly in place, and after each shaking turning the funnel bottom-side up and opening the stop-cock to relieve the pressure. Allow the two layers to separate as completely as pos-

sible, draw off the aqueous solution below, allowing it to run into the first acid solution. Transfer the ethereal solution of the malonic ester to a distilling bulb. Distil off the ether on a water-bath, using a condenser, then put in the mouth of the bulb a rubber stopper bearing a tube drawn out below to a fine capillary, which reaches nearly to the bottom of the bulb, and attach a second bulb to the side tube (see Fig. 34, 171, but omit the thermometer). Heat in the water-bath and reduce the pressure to 50 mm., or less, for fifteen minutes. This method of drying substances which boil above 190° is usually quicker and more satisfactory than the use of calcium chloride or other drying agents. Malonic ester may also be dried with advantage by allowing it to stand in a crystallizing dish in a vacuum desiccator for twenty-four hours.

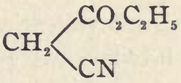
After drying, distil with a thermometer and condensing tube (see 1, p. 26). Very little passes over below 190°, and that boiling from 190°-200° will be very nearly pure malonic ester, If a very pure ester is desired, it may be distilled again, and only the portion boiling within one degree of the true boiling-point taken. Yield, 45 grams.

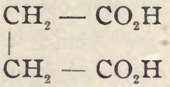
The sodium carbonate solution contains some of the acid ester. If this solution is added to the first acid solution, the acid ester separates with some ether. The ethereal solution may be separated, the ether evaporated at a gentle heat, and the residue added to the contents of the flask, in which a second saponification of the cyanacetate is to be effected. This will increase the yield to 50 grams.

Malonic ester is a colorless liquid which boils at 198°, and has a specific gravity of 1.061 at 15°. It is decomposed on heating to 150° with water, giving acetic ester, carbon dioxide, and alcohol. (For the conduct of malonic ester toward sodium ethylate and its use in syntheses, see p. 111.)

If it is desired to prepare malonic acid, after adding the potassium cyanide as directed above, continue to heat gently for half an hour, then add 120 cc. of a strong solution of sodium hydroxide (3 cc. = 1 gram NaOH), and continue to heat, replacing the water which evaporates, as long as the evolution of ammonia continues, usually about an hour. Add carefully 68 cc. of hydrochloric acid (4 cc. = 1 gram HCl), and a solution of 70 grams of calcium chloride. Filter, wash with cold water, and dry at 100°. The calcium malonate retains two molecules of water. To obtain the free acid the salt is decomposed by warming with the calculated amount of a strong solution of oxalic acid, filtering from the calcium oxalate, and evaporating to crystallization. Malonic acid melts at 134° and dissolves in about two-thirds of its weight of water at 16°. At 140°-150° it decomposes into carbon dioxide and acetic acid, a reaction characteristic of acids having two carboxyls combined with one carbon atom.

The calcium salt is almost insoluble in cold water.

The malonic ester prepared by the directions given contains some cyanacetic ester,  $CH_2\left\langle\begin{matrix}CO_2C_2H_5\\CN\end{matrix}\right.$, which does not, however interfere with its use for most synthetical purposes. If pure malonic ester is required, the calcium malonate should be prepared as directed above. This salt is thoroughly dried and mixed with four or five times its weight of absolute alcohol and dry hydrochloric acid gas passed into the mixture till the salt passes into solution. After boiling for two or three hours with a reversed condenser, most of the alcohol is distilled off under diminished pressure and the malonic ester separated as above.

56. Preparation of a Cyanide and Acid from a Halogen Derivative of a Hydrocarbon.—Succinic acid,  $\begin{matrix}CH_2 - CO_2H\\|\\CH_2 - CO_2H\end{matrix}$.

Literature.—Simpson: Ann., 118, 374; 121, 154; Nevole u. Tscherniak: Bull. soc. chim., 30, 101; Fauconnier: *Ibid*, 50, 214; Brown, Walker: Chem. News, 66, 91; Ann., 261, 115; Liebig: *Ibid*, 70, 104, 363; König: Ber., 15, 172.

50 grams ethylene bromide.
100 cc. alcohol.

34 grams potassium cyanide.
35 cc. water.

40 grams potassium hydroxide.

65 cc. concentrated hydrochloric acid.

Place in a 300 cc. flask 50 grams of ethylene bromide and 100 cc. of alcohol. Connect with an upright condenser, heat to boiling on a water-bath, and drop into the solution slowly from a dropping funnel placed in the top of the condenser, a solution of 34 grams of potassium cyanide in 35 cc. of water. After the solution has all been added, boil on the water-bath for an hour and a half. Cool, and pour off from the potassium bromide into a flask containing 40 grams of solid potassium hydroxide, cooling, if necessary, to prevent too violent a reaction at first. Rinse the residue of potassium bromide twice with a small amount of alcohol, adding the rinsings to the main portion. Boil with an upright condenser for two hours. Pour the contents of the flask into a porcelain dish, and evaporate on the water-bath till the alcohol is entirely removed. Add fifty cc. of water, and 40 cc. of concentrated hydrochloric acid, and filter. To the filtrate add 25 cc. more of concentrated hydrochloric acid, cool very thoroughly, filter off the succinic acid, and crystallize it from hot water. The yield is poor.

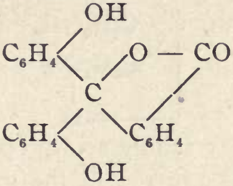
Succinic acid crystallizes from water in tabular crystals. It melts at 182°. If heated above its melting-point, it is converted into the anhydride. 100 parts of water at 0° dissolve 2.8, at 20°, 6.9 and at 50° 24.4 parts of the acid. 100 parts of alcohol at 12° dissolve 7.5 parts, and 100 parts of ether, 1.26 parts.

Ethylene cyanide is present in the above alcoholic solution and can be obtained from it as follows: Pour the solution off from the potassium bromide into a 300 cc. distilling bulb, rinse as before and distil off as much of the alcohol as possible on the water-bath. Transfer to a 100 cc. bulb, fitted with a thermometer, capillary tube, and receiving bulb, as indicated in Fig. 34,

p. 171. Distil on the water-bath under diminished pressure as long as alcohol or water comes over. Then change the receiver and distil carefully over a free flame, or in an oil-bath, with the pressure as low as possible.

Ethylene cyanide boils, under 10 mm. pressure at 147°, under 760 mm. pressure at 265°-267°, with partial decomposition. It melts at 54°. It has been suggested as a solvent for molecular weight determinations by the cryoscopic method, as it has the highest known constant, 182.6. It cannot be used for substances which ionize, however, as its ionizing power is large. Bruni, Mannelli: Z. Elektroch., 11, 860.

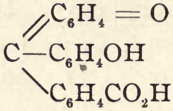
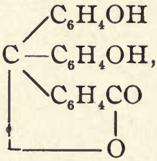
57. Preparation of a Condensation Product from Phthalic Anhydride.—Phenolphthaleïn,



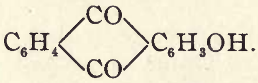
Literature.—Baeyer: Ann., 202, 68; 183, 1; Ber., 9, 1230; Knecht: *Ibid,* 15, 1068; Ann., 215, 83; (Indicator) Menschutkin: Ber., 16, 319; H. C. Jones and Allen: Am. Chem. J., 18, 377; Structure as an indicator, Orndorff: Am. Ch. J., 26, 110; Stieglitz: J. Am. Chem. Soc., 24, 590; A. A. Noyes, *Ibid,* 32, 860.

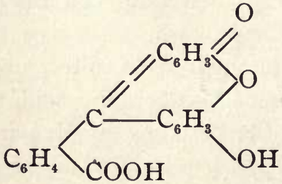
10 grams phthalic anhydride.
8 grams concentrated sulphuric acid.
20 grams phenol.

Put in a small flask 10 grams of phthalic anhydride, 8 grams of concentrated sulphuric acid, and 20 grams of crystallized phenol. Heat in an oil-bath, with a thermometer in the mixture, at 115°-120° for ten hours. Pour the hot mass into 100 cc. of boiling water, and boil till the odor of phenol disappears, filter hot, and wash. Dissolve the residue in a dilute solution of sodium hydroxide, filter, precipitate with acetic acid and a few drops of hydrochloric acid, and allow to stand for twelve hours. Dry the residue, dissolve it in 6 parts of boiling alcohol, add one-half its weight of bone-black, boil for some time, filter and wash with two parts of hot alcohol. Distil off two-thirds of the alcohol, and add a very little water. Filter, or pour off, if gummy matters separate, and precipitate the phenolphthaleïn with water, warming for a few minutes to cause it to become crystalline.

The crystalline phenol phthaleïn melts at 250°-253°. Phenolphthaleïn forms salts with alkalies, which are soluble in water with a deep red color. These solutions probably contain salts derived from the quinoid form,  $\mathrm{C}\begin{cases} =\mathrm{C_6H_4=O} \\ -\mathrm{C_6H_4OH} \\ -\mathrm{C_6H_4CO_2H} \end{cases}$. In the presence of hydrogen ions the acid which is formed rearranges at once to the tautomeric form,  which is colorless and which has only the very faintly acid properties characteristic of phenols. The solutions are red in the presence of alkalies, or normal carbonates, but colorless in the presence of bicarbonates, or free acids. Owing to its extreme sensitiveness to even weak acids, phenol phthaleïn is especially suited as an indicator for the titration of organic acids.

By heating with concentrated sulphuric acid at 200°, phenol phthaleïn is converted into hydroxyanthraquinone,



If resorcinol is used in place of phenol, and zinc chloride is used as a condensing agent, (half the weight of the phthalic anhydride), the temperature being raised to 200°-211° till the mass becomes solid, fluoresceïn,  , is formed. By treating with bromine in an alcoholic solution, this is converted into tetrabromfluoresceïn (eosin). Eosin and other similar compounds, and also anthracene derivatives which are obtained from these compounds by heating with concentrated sulphuric acid (see above), are used as dyes.

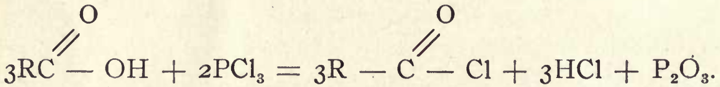
Compounds of the fluoresceïn type are only formed when the hydroxyl groups of the phenol are in the meta position and the third meta position is also free.

Chapter VIII

DERIVATIVES OF ACIDS

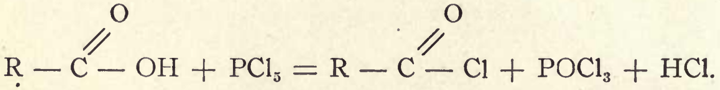
The derivatives of organic acids are of two classes: those derivatives in which the carboxyl (CO_2H) group is affected, and those in which the rest of the acid is changed. To the former class belong salts, chlorides, anhydrides, amides, and esters; to the latter, halogen derivatives, nitro derivatives, amino-acids, hydroxy-acids, and, indeed, nearly or quite all classes of derivatives which may be formed from hydrocarbons. Only the first class of derivatives will be considered in this chapter.

The *chlorides* of acids are prepared by treatment of the acid, or one of its salts, with phosphorus trichloride, phosphorus pentachloride or phosphorus oxychloride. The trichloride is usually used for the lower members of the fatty acid series, and for cases where the boiling-point of the chloride is near that of phosphorus oxychloride.



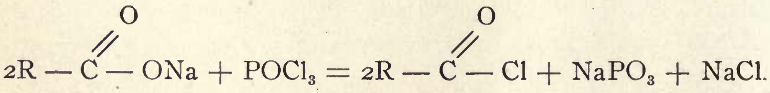
$$3\mathrm{R}\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}-\mathrm{OH}+2\mathrm{PCl_3}=3\mathrm{R}-\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}-\mathrm{Cl}+3\mathrm{HCl}+\mathrm{P_2O_3}.$$

For other cases, and especially when acids react with difficulty, phosphorus pentachloride is used.



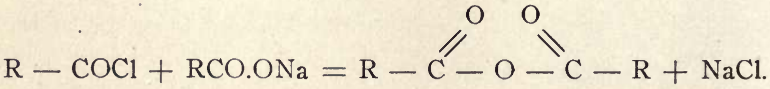
$$\mathrm{R}-\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}-\mathrm{OH}+\mathrm{PCl_5}=\mathrm{R}-\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}-\mathrm{Cl}+\mathrm{POCl_3}+\mathrm{HCl}.$$

Phosphorus oxychloride is rarely used except with the salts of acids.



$$2\mathrm{R}-\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}-\mathrm{ONa}+\mathrm{POCl_3}=2\mathrm{R}-\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}-\mathrm{Cl}+\mathrm{NaPO_3}+\mathrm{NaCl}.$$

The anhydrides of monobasic acids are usually prepared by the action of the chloride of the acid on its sodium salt.

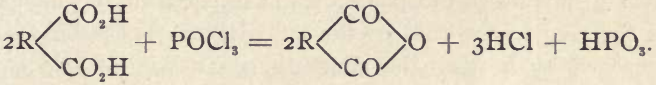


$$\mathrm{R}-\mathrm{COCl}+\mathrm{RCO.ONa}=\mathrm{R}-\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\backslash\!\backslash}{\mathrm{C}}}-\mathrm{R}+\mathrm{NaCl}.$$

In some cases an excess of the alkaline salt is treated with phosphorus oxychloride.

$$4R - CO.ONa + POCl_3 = NaPO_3 + 3NaCl + 2R{-}CO{-}O{-}CO{-}R.$$

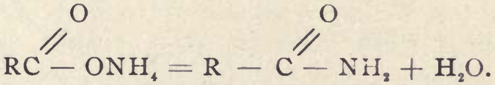
Bibasic acids in which the two carboxyl groups are separated by two carbon atoms, either in the aliphatic or aromatic series (succinic and phthalic acids and their derivatives), readily form inner anhydrides, in most cases by the action of heat alone and at temperatures below 210°. (Auwers: Ann., 285, 223.) The formation of such anhydrides can be effected at lower temperatures, and in most cases quantitatively by the use of acetyl chloride, acetic anhydride, or phosphorus oxychloride.



$$2R\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + POCl_3 = 2R\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + 3HCl + HPO_3.$$

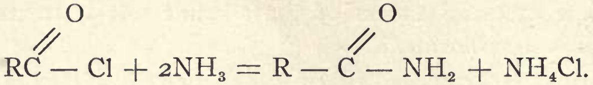
Glutaric acid and its derivatives with open chains and, apparently, the "cis" forms of cyclic derivatives, also form anhydrides by the same treatment, but isophthalic acid gives no inner anhydride.

Amides may be prepared in many cases by heating ammonium salts of acids.



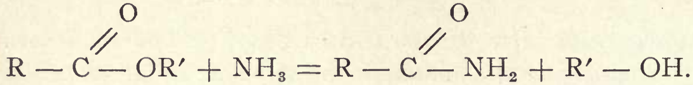
$$R\overset{O}{\overset{/\!/}{C}} - ONH_4 = R - \overset{O}{\overset{/\!/}{C}} - NH_2 + H_2O.$$

Another method, which is applicable in almost all cases where the resulting amide is difficulty soluble in water, consists in treating the acid with phosphorus pentachloride to convert it into chloride, and then adding the mixture of the chloride with phosphorus oxychloride carefully to cold concentrated aqueous ammonia, or ammonia gas may be passed into the mixture, diluted with benzene, ether, or chloroform. In some cases it is best to distil away the phosphorus oxychloride under diminished pressure before adding the chloride of the acid to the ammonia. In others the oxychloride may be decomposed by ice-water without decomposing the chloride of the acid.



$$R\overset{O}{\overset{\parallel}{C}}-Cl + 2NH_3 = R-\overset{O}{\overset{\parallel}{C}}-NH_2 + NH_4Cl.$$

Esters, on treatment with ammonia, are converted into amides:

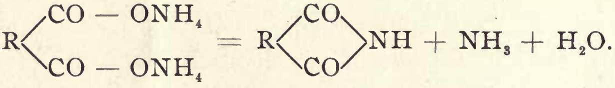


$$R-\overset{O}{\overset{\parallel}{C}}-OR' + NH_3 = R-\overset{O}{\overset{\parallel}{C}}-NH_2 + R'-OH.$$

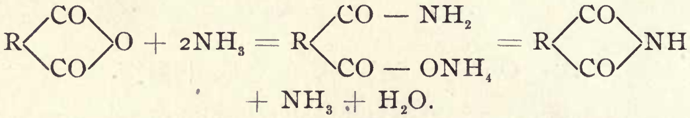
This method is seldom used, except in cases where other methods fail. (See Einhorn and Bull: Ann., **295**, 207; Noyes: Am. Chem. J., **20**, 811.)

The preparation of amides from nitriles or cyanides has been referred to on p. 108.

Acids which form inner anhydrides form also imides in which the NH group takes the place of the oxygen atom which completes the ring in the case of the anhydride. These imides may be prepared by heating the ammonium salt of the acid:



In some cases the ammonium salt of the half amide of the acid gives better results. The conversion of an anhydride into an imide by the action of ammonia, or ammonium carbonate, probably depends on the intermediate formation of such a salt:



Closely related to the amides are anilides and similar compounds, which may be considered either as amides having a hydrogen atom of the NH_2 group replaced by a hydrocarbon residue, or as an amine having a hydrogen atom of the amine group replaced by an acid radical. Anilides and similar compounds may frequently be prepared by simply heating the acid with the amine, water being eliminated more easily than in the case of the ammonium salts.

$$RCOOH + R'NH_2 = R—CO—NHR' + H_2O$$

A more general method consists in treating the amine with the chloride or anhydride of the acid, either directly, or in the presence of an aqueous solution of sodium hydroxide. ("Schotten-Baumann reaction," see 65, p. 154.)

Alkyl or aryl cyanides may also be considered as derivatives of acids and as such they are called *nitriles*. From this point of view they may be prepared by treating the amide of an acid with phosphorus pentoxide:

$$R—CONH_2 + P_2O_5 = R—CN + 2HPO_3.$$

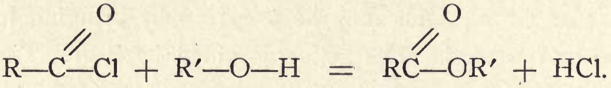
The preparation of cyanides from alkyl halides and in other ways has already been considered, (p. 107).

Esters of strong acids may be prepared by bringing together the acid and alcohol. The action is aided by heat. The reaction is, however, a reversible one and proceeds only till an equilibrium is established between the amounts of ester, water, alcohol, and acid present. For equivalent weights of acid and alcohol, the per cent. of ester formed, when equilibrium is reached, is characteristic of the acid and alcohol in question, and varies greatly in different cases. Primary alcohols form esters more quickly and in larger amount than secondary, and secondary than tertiary. In a similar manner acids with a primary carboxyl ($R—CH_2CO_2H$) form esters more quickly than those with secondary carboxyl, and the latter more quickly than those with a tertiary carboxyl. These facts may be used to determine the structure of the alcohols and acids (Menschutkin, see third edition of Beilstein I, 218 and 389. For a practical application in determining the structure of an acid see Noyes: Am. Chem. J., 18, 685).

The amount of an acid which will be converted into an ester is increased by the use of a larger amount of the alcohol, in accordance with the law of mass action, which applies to all reversible processes, that the increase of the amount of one of the reacting substances increases the amount of product or products (in this case ester and water) which result from its action on other substances present. It follows that an excess of the alcohol should be used when the acid is rare or expensive, and an excess of the acid when the alcohol is valuable.

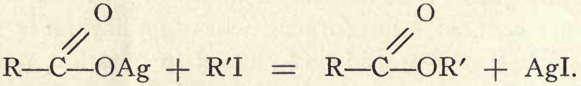
In most cases esterification is very much hastened by the addition of hydrochloric or sulphuric acid to a mixture of an organic acid and alcohol. It was formerly supposed to be necessary to saturate the mixture with dry hydrochloric acid gas, but Emil Fischer has shown (Ber., 28, 3252), that a comparatively small amount of hydrochloric or sulphuric acid may frequently be used with better advantage.

Esters may, in most cases, be readily prepared from the chlorides of acids by treatment with an alcohol. (See Baeyer: Ann., 245, 140.)



$$\mathrm{R{-}\overset{\overset{O}{/\!/}}{C}{-}Cl + R'{-}O{-}H = R\overset{\overset{O}{/\!/}}{C}{-}OR' + HCl.}$$

They may also be prepared by treating a silver salt of an acid with an alkyl iodide,



$$\mathrm{R{-}\overset{\overset{O}{/\!/}}{C}{-}OAg + R'I = R{-}\overset{\overset{O}{/\!/}}{C}{-}OR' + AgI.}$$

For methyl esters dimethyl sulphate and the sodium salt of an acid may be used.

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58. Preparation of an Acid Chloride.—Acetyl chloride, $CH_3.COCl$. (Ethanoyl chloride.)

Literature.—Béchamp: Jsb. d. Chem., *1855*, 504; *1856*, 427; J. prakt. Chem., 65, 495; Thorpe: J. Chem. Soc., 1880, 37, 186; Bothamley, Thompson: Chem. News., *1890*, 62, 191; Gerhardt: Ann., 87, 63.

100 grams acetic acid (glacial).

80 grams phosphorus trichloride.

Arrange a 300 cc. distilling bulb, condenser and receiver as indicated in Fig. 33.

All of the apparatus must be absolutely dry, and the side tube of the receiver should be connected with a tube which will deliver the hydrochloric acid evolved immediately over the surface of some water in a bottle. Place in the distilling bulb 100 grams (96 cc.) of glacial acetic acid, and add through the dropping funnel 80 grams of phosphorus trichloride. Warm for a short time, gently, till the evolution of hydrochloric acid nearly ceases and the liquid separates in two layers. Then distil from a water-bath as long as anything comes over. The distillate usually contains some phosphorus trichloride. If a product entirely free from phosphorus is required, add two or three grams of powdered, dry, sodium acetate, allow to stand over night, and distil again from the water-bath, collecting the portion boiling at 50°-56°. Yield 80 to 90 grams.

Acetyl chloride is a colorless liquid with a very disagreeable odor. It boils at 50.9°, and has a specific gravity of 1.1051 at 20°. It decomposes rapidly with water or moist air and must be kept in tightly closed, glass-stoppered, or sealed bottles.

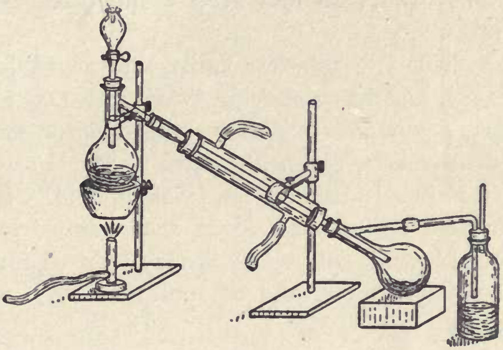
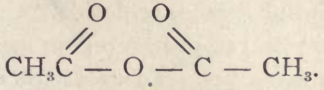


Fig. 33.

Acetyl chloride reacts readily with almost all bodies containing either an alcoholic hydroxyl, or an amine group. In both cases a hydrogen atom of the group is replaced by the acetyl group, C_2H_3O. The resulting compounds are, in many cases, crystalline and difficultly soluble in water, and hence well adapted for the characterization of substances of these two classes.

59. **Preparation of an Anhydride of an Acid.**—Acetic anhydride,



$CH_3\overset{\overset{O}{/\!/}}{C} — O — \overset{\overset{O}{\backslash\backslash}}{C} — CH_3$. (Ethanoic anhydride.)

Literature.—Gerhardt: Ann., (*1852*), 82, 131; 87, 149.

60 grams dry sodium acetate.

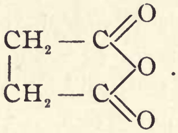
50 grams acetyl chloride.

Place in a dry, 200 cc. flask, 60 grams of freshly fused, dry, powdered sodium acetate, and connect with an upright condenser. Add, in small portions, through the condenser, 50 grams of acetyl chloride, shaking vigorously after each addition. Warm on a water-bath as long as any acetyl chloride condenses and runs back. Then connect the flask with the condenser in the usual manner by means of rubber stoppers and a bent tube, and distil slowly with a free flame, holding the burner in the hand. Collect the portions boiling at 130°-142°. Add to the distillate two or three grams of dry sodium acetate and distil again. Yield 40 to 50 grams.

Acetic anhydride is a colorless liquid with an unpleasant odor. It boils at 138°, and has a specific gravity of 1.08 at 15°.

When most compounds containing alcoholic or amine groups acetic anhydride reacts, giving the same products as acetyl chloride. The reaction is usually less violent, and, of course, no hydrochloric acid is formed. Since acetic anhydride does not react very quickly with cold water, it may be used for the Schotten-Baumann reaction (**65** and **66**, pp. 154, 155), while acetyl chloride cannot.

60. Preparation of the Anhydride of a Bibasic Acid.—Succinic anhydride,



Literature.—Gerhardt u. Chiozza: Ann., **87**, 293; Anschütz: Ber., **10**, 1883; Ann., **226**, 8; Volhard: *Ibid*, **242**, 150; Auwers: *Ibid*, **285**, 223.

20 grams succinic acid.

13 grams phosphorus oxychloride.

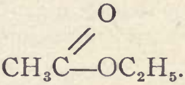
Place in a small flask 20 grams (2 mols.) of dry succinic acid. Add 13 grams (1 mol.) of phosphorus oxychloride. Connect with an upright condenser, and warm gently on an asbestos plate so long as hydrochloric acid escapes. To avoid the escape of the acid into the room connect the top of the condenser with a tube which will deliver the gas just above the surface of water in a bottle. When acid ceases to escape, transfer to a 50 cc.

distilling bulb, connect with an air condensing tube, and distil. When the drops coming over solidify easily, remove the condensing tube and distil slowly into a small flask without any condenser. Crystallize the anhydride from chloroform. Yield almost quantitative.

Instead of phosphorus oxychloride, 12 grams of phosphorus pentachloride may be used but, in that case, the mixture should be warmed on the water-bath till it becomes liquid before placing it on the asbestos plate over the free flame.

Succinic anhydride crystallizes from chloroform or acetic anhydride in needles, which melt at 119.6°. It boils at 261°. It may also be crystallized from absolute alcohol, but on boiling for some time with absolute alcohol it is converted into the mono-ethyl ester of succinic acid.

61. **Preparation of an Ester**—Ethyl acetic ester, (Acetic ester).


$CH_3\overset{O}{\overset{/\!/}{C}}—OC_2H_5.$ (Ethyl Ester of Ethanoic Acid.)

Literature.—Geuther: Jsb. d. chem., *1863*, 323; Frankland, Duppa: Ann., 138, 205; Markownikoff: Ber., 6, 1177; Pabst: Bull. soc. chim., 33, 350.

25 cc. alcohol.
25 cc. concentrated sulphuric acid.
200 cc. alcohol.
200 cc. glacial acetic acid.

Place in a 250 cc. distilling bulb 25 cc. of alcohol, and 25 cc. of concentrated sulphuric acid. Put in the mouth of the bulb a stopper bearing a separatory funnel, the stem of which reaches nearly to the bottom of the bulb, and a thermometer which dips in the mixture. (See ethyl ether, p. 81.) Connect with a condenser and heat carefully to 130°-135°. Run in slowly a mixture of 200 cc. of glacial acetic acid and 200 cc. of alcohol, regulating the flow and the flame so that the temperature remains at about 135°. Shake the distillate in a flask with a concentrated sodium carbonate solution till it no longer reacts acid, separate the aqueous solution by means of a separatory funnel, add a solution of 50 grams of calcium chloride in 50 grams of water, shake, and separate again, to remove alcohol which it contains. Dry the acetic ester by allowing it to stand over night with a little fused calcium chloride, and fractionate. The portion boiling at 72°-78° is nearly pure. For use in the preparation of acetoacetic ester it should be allowed to stand a day with one-fifth of its weight of granular calcium chloride and filtered. Yield 80-90 per cent. of the theory.

Acetic ester boils at 77°, and has a specific gravity of 0.9239 at $\frac{0°}{4°}$, and of 0.8300 at $\frac{75.5°}{4°}$. It dissolves in 17 parts of water at 17.5°, 28 parts of the ester dissolve one part of water It is easily saponified by boiling with alkalies, and is slowly saponified by merely standing with water.

62. Saponification of an Ester with Sodium Hydroxide and Detection of the Alcohol Formed.

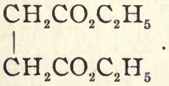
Literature.—H. Meyer: Analyse und Konstitutionsermittelung organischer Verbindungen, p. 510; Nernst: Theoretical Chemistry, Translation of the 4th German edition, p. 550.

2 grams acetic ester.

15 cc. sodium hydroxide (10 per cent.).

Put 2 grams of acetic ester and 15 cc. of ten per cent. sodium hydroxide in a small flask, connect with an upright condenser and boil for fifteen minutes, cool, transfer to a 50 cc. distilling bulb and distil over about 6 cc. Put the distillate in a very small distilling bulb and distil about 3 cc. To the distillate add dry potassium carbonate till the alcohol separates on top. Transfer the upper layer to a small distilling bulb and determine the boiling-point, boiling it with a very small flame and using as small a distilling bulb as possible. See pp. 26 and 269. For the saponification of a fat see 48, p. 121. For the saponification of a cyanide see 52 p. 133 and 140.

63. Preparation of an Ester of a Bibasic Acid.—Ethyl succinic ester,



$$\begin{array}{l} CH_2CO_2C_2H_5 \\ | \\ CH_2CO_2C_2H_5 \end{array}.$$

Literature.—Weger: Ann., 221, 89; Fehling: *Ibid,* 49, 186, 195; Perkin: J. Chem. Soc., 45, 515 (*1884*); Crum Brown, Walker: Ann., 261, 115.

100 grams succinic acid.
170 cc. alcohol.
5 cc. concentrated sulphuric acid.

In a 300 cc. flask put 100 grams of succinic acid, 170 cc. of alcohol and 5 cc. of concentrated sulphuric acid. Heat for two hours on a water-bath with an upright condenser or condensing tube. Cool, and pour into a large flask containing 25 grams of sodium bicarbonate and 150 of water. Shake thoroughly, and separate the ester. Wash it once with a little water, dry as directed for malonic ester (see p. 138), and fractionate. Yield good.

Succinic ethyl ester boils at 217°-218°, and has a specific gravity of 1.0475 at 25.5°.

64. Preparation of an Ester by Means of Phosphorus Pentachloride and Alcohol.—Benzoic ethyl ester, $C_6H_5CO_2C_2H_5$.

Literature.—Baeyer: Ann., 245, 140; Liebig: *Ibid*, 65, 351; E. Fischer, Speier: Ber., 28, 1150, 3255.

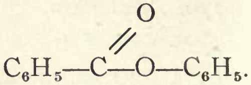
10 grams benzoic acid.
21 grams phosphorus pentachloride.
50 cc. alcohol.

Put in a small flask 10 grams benzoic acid, and 21 grams of phosphorus pentachloride. Connect with a tube which will deliver the hydrochloric acid evolved just above the surface of water in a bottle. Warm on a water-bath till all is liquid. Cool and pour carefully into 50 cc. of alcohol. Cool thoroughly, add 100 cc. of water and enough ether to bring the benzoic ester to the surface. Separate, wash with a solution of sodium carbonate to remove acid, dry the ethereal solution by allowing it to stand for several hours with dry potassium carbonate, pour off, or filter, and distil from a small distilling bulb.

Other methods of preparing benzoic ester are more suitable, and this method is only given as an illustration of a method which is quite generally applicable. The yield is almost quantitative, if care is used.

Benzoic ester boils at 211°, and has a specific gravity of 1.0502 at 16°.

65. Preparation of the Benzoyl Derivative of a Phenol—Schotten—Baumann Reaction.—Phenyl benzoate, $C_6H_5—\overset{O}{\overset{/\!\!/}{C}}—O—C_6H_5$.

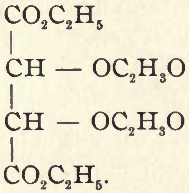


Literature.—Baumann: Ber., 19, 3218; Udranszky and Baumann: *Ibid*, 21, 2744; Hinsberg: *Ibid*, 23, 2962; Schotten: *Ibid*, 17, 2545.

Dissolve about one-half gram of phenol in 5 cc. of water, add three-fourths gram of benzoyl chloride and a little caustic soda, enough so that the solution remains alkaline after warming and shaking till the odor of benzoyl chloride has disappeared. On cooling and standing the phenyl benzoate solidifies, and, after filtering off and washing, may be crystallized from a little alcohol. It melts at 69°.

This reaction, which is generally applicable to alcohols, phenols, and to primary and secondary amines, and in which acetic anhydride, sulphonechlorides and other similar compounds may be used instead of benzoyl chloride, is especially useful in converting liquid or easily soluble bodies into solid, difficulty soluble derivatives for purposes of identification.

66. Preparation of the Ester of a Hydroxy Acid and of an Acetyl Derivative.—Di-acetyl tartaric ethyl ester,



$$\begin{array}{l} CO_2C_2H_5 \\ | \\ CH — OC_2H_3O \\ | \\ CH — OC_2H_3O \\ | \\ CO_2C_2H_5. \end{array}$$

Literature.—Landolt: Ann., 189, 324; Anschütz: Ber., 18, 1397; Wislicenus: Ann., 129, 184; Perkin: A Supl., 5, 285; J. Chem. Soc., 51, 369 (*1887*); E. Fischer: Ber., 28, 3255.

25 grams tartaric acid.
120 cc. absolute alcohol.
1 gram hydrochloric acid gas.

Put 25 grams of tartaric acid in a 200 cc. distilling bulb, add 120 cc. of absolute alcohol, and pass into the bulb about one gram of hydrochloric acid gas. The gas may be generated in a small flask from salt and concentrated sulphuric acid diluted with one-fourth of its volume of water, or by dropping concentrated sulphuric acid into commercial hydrochloric acid, and the amount can be determined by placing the bulb in a beaker on one pan of a balance, which is sensitive to about one-tenth gram. Close the side tube of the bulb with a bit of rubber tubing and a glass rod, and place in the mouth of the bulb a stopper and tube to act as an air condenser. Heat for 2 to 3 hours on a water-bath, inclining the bulb in such a manner that the vapors which condense in the side tube will run back into the bulb. Adjust a capillary tube and stopper, and a second bulb to collect the distillate, as on p. 171 and distil the excess of alcohol and the water formed under gradually diminishing pressure, and finally dry for fifteen minutes under as low a pressure as can be secured and with the bulb immersed in a boiling water-bath. Add 80 cc. of absolute alcohol, and one gram of hydrochloric acid, and heat as before with an air condenser for two hours. By the removal of the water formed by the esterification, and a second treatment with fresh alcohol a much more complete conversion can be secured. Distil the alcohol and water as before and then distil from an oil-bath or with the free flame under as low a pressure as can be secured and with a thermometer (see p. 171). The portion boiling at 160°-180° under 30 mm. pressure will consist of nearly pure di-ethyl tartaric ester. Yield 23-26 grams.

The ester boils at

280° under a pressure of 760 mm.
232° under a pressure of 197 mm.
162° under a pressure of 19 mm.
157° under a pressure of 11 mm.

It has a specific gravity of 1.2059 at 20°

3 grams di-ethyl tartaric ester.
5 grams acetic anhydride.
30 cc. sodium hydroxide (10 per cent.).

Place in a small flask 3 grams of di-ethyl tartaric ester, add five grams of acetic anhydride and then, in small portions, with constant shaking, 30 cc. of a 10 per cent. solution of sodium hydroxide. As soon as the odor of the acetic anhydride has disappeared, filter off the acetyl derivative, if it solidifies, wash it with water and recrystallize it from alcohol, dissolving in a very little hot alcohol, and adding water till the solution begins to become turbid.

If the acetyl compound fails to solidify at first, it will usually do so on standing in a cool place for a day or two. If some of the crystallized compound is at hand, the addition of a crystal will be of service.

Di-acetyl tartaric ethyl ester melts at 67°, and boils at 291°-292° under 727 mm., or at 229°-230° under 100 mm.

Very considerable historical interest attaches to the substance, because by means of it the structure of tartaric acid was first clearly established.

67. Preparation of an Amide by Heating the Ammonium Salt of an acid.—Acetamide, $CH_3—CONH_2$.

Literature.—Letts: Ber., 5, 669; Hofmann: *Ibid,* 15, 978; v. Nencki, Leppert: *Ibid,* 6, 903; J. Schultze: J. prakt. Chem., (1883), N. F., 27, 514.

50 grams glacial acetic acid.
55 to 60 grams ammonium carbonate.

Warm 50 grams of acetic acid gently in a porcelain dish and add powdered ammonium carbonate till a little of the mixture, on dilution with water, shows an alkaline reaction with litmus. Prepare two sealing tubes about 2 to 2.5 centimeters in internal diameter, and with walls 2 to 3 mm. thick. In closing the ends of the tubes, and also in sealing after they have been filled, the glass must be so thoroughly softened as to sink together somewhat, and must not be drawn so rapidly as to become thin at any point. Warm the sealing tubes gently over the flame, and heat the ammonium acetate till it becomes liquid. Transfer it to the tubes, using a thistle tube or funnel with a long stem so that the tubes are not wet near the point where they are to be sealed. The tubes, when sealed, should not be more than three-fourths full. Seal the tubes carefully, and when cold put them in a bomb oven and heat for five hours at 220°-230°. Cool. Open the tubes and transfer the mixture to a distilling bulb and subject it to fractional distillation, using an air condensing tube (see p. 26). Collect the portion boiling at 180°-230° in a beaker. Cool thoroughly, and spread on porous porcelain to remove liquid impurities. The portion remaining will be nearly pure acetamide. The pure compound may be obtained by crystallization from benzene or chloroform. Yield about 25 grams.

Pure acetamide consists of colorless, odorless, rhombohedral crystals, which melt at 82°. It boils at 222°. It is easily soluble in alcohol and in water, difficultly soluble in ether and benzene.

Acetamide is easily saponified by alkalies. It is converted into methylcyanide (acetonitrile) by warming for a short time with phosphorus pentoxide and distilling. An aqueous solution of acetamide dissolves mercuric oxide with the formation of the compound, $(CH_3CONH)_2Hg$. The hydrogen of the amide group may also be replaced by bromine or by other halogen atoms. Acetamide forms unstable salts with hydrochloric acid and with nitric acid.

68. Preparation of an Acyl Derivative of an Amine.—Acetanilide, $C_6H_5NH.C_2H_3O$.

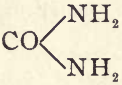
Literature.—Gerhardt: Ann., 87, 164; Williams: *Ibid,* 131, 288; Witt: Dissertation, (Zürich, 1875), 12, Williams: J. Chem. Soc., 17, 106, (*1864*).

25 grams aniline.
35 grams glacial acetic acid.

Put in a 200 cc. flask 25 grams of aniline and 35 grams of glacial acetic acid. Place in the mouth of the flask a stopper bearing a tube one cm. in diameter and 50 cm. long. Heat on a thin asbestos paper on a wire gauze, and adjust the flame so that the vapors of the acetic acid condense about two-thirds of the way up the tube. As water is formed during the reaction, it will gradually escape from the top of the tube, and this hastenes the reaction. If the apparatus cannot be conveniently placed in a hood, the top of the tube should be bent over, and a flask placed under it to collect the dilute acid which escapes. After boiling for 4 to 5 hours, pour carefully, with stirring, into 400 cc. of water, filter when cold, and recrystallize from hot water, dilute alcohol, or from benzene. Yield about 80 per cent. of the theory.

Acetanilide (known in medicine as antifebrin) melts at 116°, and boils at 304°. It dissolves in 189 parts of water at 6°. It is easily soluble in hot water, alcohol, ether, and benzene. It may be saponified either by boiling with caustic potash or concentrated hydrochloric acid.

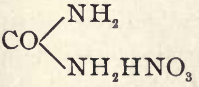
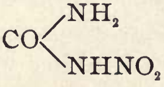
69. Preparation of an Amide from the Chloride of an Acid.—

Urea,  $CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, Carbamide.

Literature.—Wöhler: Berz. Jsb., 12, 266 (*1828*); Natanson: Ann., 98, 289; Basarow; J. prakt. Chem, [2], 1, 283; Mixter: Am. Chem. J., 4, 35; Millon: Ann. chim. phys., [2], 8, 235; Schmidt: Ber., 10, 191; Duggan: Am. Chem. J., 4, 47; Schmidt: Z. anal. Chem., 1, 242.

10 cc. solution of phosgene in toluene (20 per cent.).
15 cc. ammonia (0.96).

Put in a small flask 15 cc. of ammonia and add in three or four portions, shaking and cooling after each addition, 10 cc. of a twenty per cent. solution of carbonyl chloride, $COCl_2$ (phosgene), in toluene. The solution should now react alkaline. Pour the mixture into a porcelain dish, and evaporate to dryness on the water-bath. Put the residue into a dry test-tube, add about 10 cc. of alcohol, and boil. Cool, pour off through a filter, and repeat the same treatment twice. Evaporate the alcoholic solution to dryness. The residue will now consist mainly of urea with a little ammonium chloride. About one gram should be obtained. Crystallize from a little amyl alcohol.

Urea crystallizes in long prisms or thick needles. It melts at 132°. It is easily soluble in water. 100 parts of alcohol dissolve 5.06 parts at 19.5°. From not too dilute aqueous solutions it is precipitated in the form of the nitrate,  $CO\left\langle\begin{matrix}NH_2\\NH_2,HNO_3\end{matrix}\right.$, on the addition of nitric acid. The nitrate is very difficultly soluble in nitric acid, and is converted into nitrourea,  $CO\left\langle\begin{matrix}NH_2\\NHNO_2\end{matrix}\right.$, by cold concentrated sulphuric acid. (See p. 94). Urea forms double compounds with many salts and metallic oxides, and, also, compounds in which its hydrogen is replaced by metals. It is decomposed by alkaline hypobromites with liberation of nitrogen, a property used for its quantitative determination.

Concentrated solutions of alkalies decompose it on boiling, with the formation of a carbonate and ammonia. Acids decompose it more rapidly.

70. Preparation of an Amide by means of Phosphorus Pentachloride and Ammonia.—Phenyl sulphonamide, $C_6H_5SO_2NH_2$.

Literature.—Mitscherlich: Ann. phys. (Pogg.), **31**, 283, 631; Stenhouse: Ann., **140**, 284; Gattermann: Ber., **24**, 2121; Michael, Adair: Ber., **10**, 585; Gerhardt, Chancel: J., *1852*, 434; v. Meyer, Ador: Ann., **159**, 11; Limpricht: *Ibid*, **221**, 206.

100 cc. fuming sulphuric acid (sp. gr. 1.87).
50 cc. benzene

350 cc. water.
50 grams acid sodium carbonate.
100 grams salt.

20 grams crude sodium benzene sulphonate.
20 grams phosphorus pentachloride.

70 cc. ammonia (sp. gr. 0.90).

To 100 cc. of fuming sulphuric acid, containing 5 to 8 per cent. of the anhydride (sp. gr. 1.87 at 15°), in a 300 cc. flask, add, in small portions, 50 cc. of benzene, shaking vigorously after each addition and keeping the temperature below 50° by occasional cooling. When the benzene has all dissolved, pour slowly into 350 cc. of water, cool, and filter from any diphenyl sulphone, $(C_6H_5)_2SO_2$, which separates. Partly neutralize the acid by adding, carefully, 50 grams of acid sodium carbonate (baking soda), then add 100 grams of common salt, warm till it dissolves, filter and cool, with stirring. As soon as the sodium benzene sulphonate has separated completely, filter on a plate and suck dry. Moisten with a saturated solution of salt and suck dry again. Dry the salt on a plate of porous porcelain. Yield

40 to 50 grams of the salt. The salt can be crystallized from alcohol if desired, but is already pure enough for most purposes.

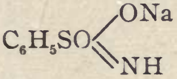
Place in a 100 cc. flask 20 grams of phosphorus pentachloride (weigh in the hood and avoid exposure to the air as far as possible), add 20 grams of crude sodium benzene sulphonate, dried at 120°, close the flask with a perforated rubber stopper bearing a tube which will deliver the hydrochloric acid evolved just above the surface of water in a bottle or flask. Warm on the water-bath as long as hydrochloric acid is evolved. Cool. Pour the contents of the flask, in small portions, into 70 cc. of ammonia (0.90 sp. gr.) contained in a 200 cc. flask, cooling thoroughly after each addition. Filter, wash with cold water, and crystallize from hot water or from dilute alcohol. Yield 12 to 15 grams.

If benzene sulphonechloride is desired, the liquid product obtained by the action of the pentachloride on sodium benzene sulphonate may be poured in small portions into 200 cc. of cold water, and shaken with the latter for some time to decompose the phosphorus oxychloride, the sulphonechloride taken up with ether, and after drying with calcium chloride and distilling off the ether, distilled under diminished pressure.

Benzene sulphonechloride melts at 145° and boils with decomposition at 246°. Under 10 mm. pressure it boils at 120°. It has a specific gravity of 1.378 at 23°.

It may be used to distinguish the three classes of amines (Hinsberg: Ber., 23, 2963). With primary amines it gives alkyl-sulphonamides, $C_6H_5SO_2NHR$, which are soluble in alkalies, with secondary amines it gives dialkyl-sulphonamides $C_6H_5SO_2NRR'$, which are insoluble in alkalies, and with tertiary amines it does not react. The compounds with primary and secondary amines may usually be prepared by the Schotten-Baumann reaction.

Benzene sulphonamide crystallizes in needles from water, or in leaflets from alcohol. Both melt at 147°-148°. (Hybbeneth gives 156°.) It is easily soluble in alcohol and ether, difficultly soluble in cold water. The hydrogen of the amide group can be replaced by metals, hence the sulphonamides are soluble in alkalies, and some of them are quite soluble in a solution of sodium carbonate. It is probable that the amide dissolves in the "pseudo" form,



$\mathrm{C_6H_5SO}\begin{matrix}\diagup\mathrm{ONa}\\ \diagdown\!\!\diagdown\mathrm{NH}\end{matrix}$.

71. Phenyl Cyanide, C_6H_5CN. Benzonitrile.

Literature.—Laurent, Gerhardt: Jsb. d. chem., *1849*, 327; Wöhler: Ann., 192, 362; Henry: Ber., 2, 307; Letts: *Ibid*, 5, 673; Merz: Z. Chem., *1868*, 33; Merz, Weith: Ber., 8, 918; 10, 749; Lach: *Ibid*, 17, 1571; Sandmeyer: *Ibid*, 17, 2653.

15 grams benzoyl chloride.
60 cc. ammonia (sp. gr. 0.96).
10 grams benzamide.
15 grams phosphorus pentoxide.

Put in a flask 15 grams of benzoyl chloride, add 60 cc. of ammonia (10 per cent.), and shake vigorously till the chloride dissolves, which should take only a minute or two. Cool at once and thoroughly. Filter off the benzamide which separates, wash it till free from ammonium chloride, and dry in the air or on the water-bath. 11 grams of pure benzamide should be obtained.

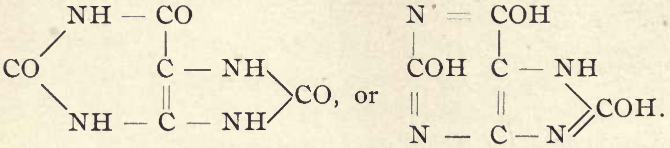
Put in a small distilling bulb 10 grams of benzamide, and 15 grams of phosphorus pentoxide, and mix as thoroughly as possible by shaking. Heat in an oil-bath at 220°-240° as long as phenyl cyanide distils over. A condenser is not necessary, but the cyanide may be collected in a small flask or test-tube as it distils. Yield 6 to 7 grams.

Most amides lose water when heated with phosphorus pentoxide, and are converted into the corresponding cyanides or nitriles.

Benzamide crystallizes in monoclinic plates, or in leaflets which melt at 128°. It is difficultly soluble in cold water, easily soluble in alcohol.

Phenyl cyanide is a colorless oil which solidifies in a freezing mixture of ether and solid carbon dioxide, and melts at —17°. It boils at 190.7°, and has a specific gravity of 1.0084 at 16.8°.

72. Uric Acid.



Literature.—Liebig and Wöhler: Ann., 26, 245; Wöhler: Ann., 70, 229; 88, 100; Arppe: *Ibid,* 87, 237; Goesmann: Ann., 99, 374; Gibbs: Chem. Z. *1869*, 729; Am. J. Sci., 48, 215 (*1869*); Ann. Supl., Bd., 7, 324; Horbaczewski: Ber., 15, 2678; Behrend u. Roosen: Ber., 21, 999; Ann., 251, 235, Formanek: Ber., 24, 3419; Zabelin: Ann. Supl. Bd., 2, 313; Fresenius: Z. anal. Chem., 2, 456; Salkowski: *Ibid,* 16, 373; E. Fischer: Ber., 17, 1785; 30, 549.

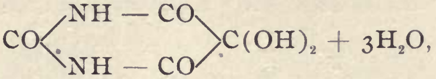
1 liter urine.
25 cc. concentrated hydrochloric acid.

Add to one liter of urine 25 cc. of concentrated hydrochloric acid and allow to stand in a cool place for two days. Decant the liquid from the crystals of uric acid and wash them by decantation. Transfer to a test-tube, dissolve in the smallest possible amount of 5 per cent. sodium hydroxide, add a drop of a solution of potassium pyrochromate and boil, then add a little bone-black, shake, and filter. Precipitate the uric acid with hydrochloric acid, allow to separate completely, filter, and wash. In working with larger amounts of uric acid the amount of the pyrochromate should be five per cent. of that of the uric acid, and after the second precipitation the uric acid, which is slightly yellow, should be warmed several times with strong hydrochloric acid, till it is perfectly white. (Gibbs: *Loc. cit.*)

The yield from one liter of urine will usually be one-half a gram or less.

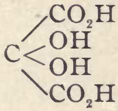
Uric acid forms a white crystalline powder, which is almost insoluble in water, alcohol, and ether. It dissolves in alkalies with the formation of salts in which two atoms of hydrogen are replaced by the metal. Carbon dioxide precipitates from such solutions difficultly soluble acid salts, a property used in the preparation of the acid from guano. It is precipitated from its solutions by an ammoniacal solution of silver nitrate. If a little uric acid is moistened with nitric acid, and the solution evaporated on the water-bath, the residue dissolves in ammonia to an onion-red solution, which becomes violet on adding sodium hydroxide ("murexide reaction").

Nitric acid oxidizes uric acid to alloxan,



$$CO\left\langle\begin{matrix}NH-CO\\NH-CO\end{matrix}\right\rangle C(OH)_2 + 3H_2O,$$

and the latter is decomposed by alkalies into urea and dihydroxymalonic acid (mesoxalic acid),



$$C\left\langle\begin{matrix}CO_2H\\OH\\OH\\CO_2H\end{matrix}\right. .$$

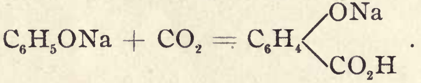
The structural formulas given above are based, in part, on these reactions.

Chapter IX

HYDROXY AND KETONIC ACIDS

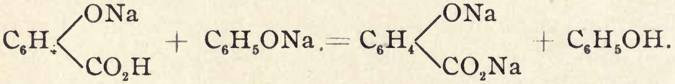
Hydroxy acids may be prepared by several of the methods used for the preparation of alcohols, as for instance: by the treatment of a halogen derivative of an acid with water or an alkali, or with silver oxide and water; by the treatment of an amino acid with nitrous acid; or by the oxidation of an unsaturated acid with potassium permanganate, giving a dihydroxy acid. (See pp. 64, 65.)

Ortho- and para-hydroxy acids may be prepared from phenols by heating a sodium or potassium salt of a phenol with carbon dioxide (Kolbe's Synthesis). It was formerly supposed that a phenyl sodium carbonate is at first formed but Tijmstra has shown (Ber., 38, 1375) that the reaction consists at first in the direct addition of the phenolate to carbon dioxide:



$$C_6H_5ONa + CO_2 = C_6H_4\left\langle\begin{matrix}ONa\\ CO_2H\end{matrix}\right. .$$

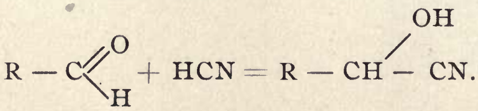
If the reaction is carried out in an autoclave under pressure it may be made nearly complete, while at atmospheric pressure the compound formed reacts with another molecule of the phenolate and phenol distils away:



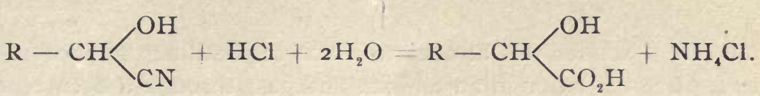
$$C_6H_4\left\langle\begin{matrix}ONa\\ CO_2H\end{matrix}\right. + C_6H_5ONa = C_6H_4\left\langle\begin{matrix}ONa\\ CO_2Na\end{matrix}\right. + C_6H_5OH.$$

With sodium phenolate the carboxyl enters chiefly in the ortho position, giving salicyclic acid, while with potassium phenolate para-hydroxy benzoic acid is formed.

Cyanhydrines may be prepared by the addition of nascent hydrocyanic acid to an aldehyde or ketone. The cyanhydrine may be saponified to an α-hydroxy acid.



$$R - C\left\langle\begin{matrix}O\\ H\end{matrix}\right. + HCN = R - \overset{OH}{CH} - CN.$$



$$R - CH\left\langle\begin{matrix}OH\\CN\end{matrix}\right. + HCl + 2H_2O = R - CH\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right. + NH_4Cl.$$

Under the influence of sodium ethylate some esters may be condensed to form esters of ketonic acids, of which acetoacetic ester and succinylosuccinnic ester may be considered types (see p. 109).

When a compound contains a methylene (CH_2) or methine (CH) group which is combined with two carboxyl groups, as in acetoacetic ester or malonic ester or between a carboxyl and a cyanogen group, as in cyanacetic ester it will usually react with sodium ethylate in the "enol" form giving a sodium salt which will, in turn, add an alkyl group in such a manner as to practically replace the hydrogen of the methylene or methine group by the allyl radical (see p. 111). The decompositions of acetoacetic ester and of malonic acid and their derivations have already been considered (p. 112).

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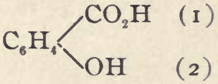
73. Preparation of a Hydroxy Acid by Treatment of the Sodium Salt of a Phenol with Carbon Dioxide (Kolbe's Synthesis).—Salicylic acid, $C_6H_4\left\langle\begin{matrix}CO_2H & (1)\\OH & (2)\end{matrix}\right.$ (*o*-hydroxybenzoic acid).



Literature.—Gerhardt: Ann., 45, 21; Köhler: Ber., 12, 246; Barth: Ann., 154, 360; Hübner: *Ibid,* 165, 1; Gerland: *Ibid,* 86, 147; Kolbe, Lautemann: *Ibid,* 115, 201; Kolbe: J. prakt. Chem., [2], 10, 93; Hentschel: *Ibid,* [2], 27, 41; Schmitt: *Ibid,* [2], 31, 407; Reimer, Tiemann: Ber., 9, 423, 824; 10, 213; Tijmstra: *Ibid,* 38, 1375.

12.5 grams sodium hydroxide.
30 grams phenol.
20 cc. water.

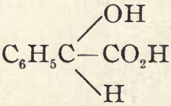
Dissolve 12.5 grams of sodium hydroxide in 20 cc. of water in a porcelain, or better in a nickel dish. Add, in portions, 30 grams of crystallized phenol. Fasten the dish firmly by means of a clamp and, with the burner in the hand and in constant motion, heat and stir carefully till a thoroughly dry powder is obtained. Transfer this at once to a 100 cc. distilling bulb, or retort, place the latter in an oil-bath and pass through it a current of dry hydrogen, while the bath is heated to 140° for half an hour.

The salt should be so dry that it does not sinter together during this part of the process. Allow the oil-bath to cool to 110°, and pass a current of dry carbon dioxide through the bulb for one hour. Then allow the temperature to rise at the rate of about 20° an hour till a temperature of 200° is reached, and heat finally for an hour at that temperature, continuing a slow current of carbon dioxide. The side tube of the distilling bulb should be heated gently, once in a while, to melt the phenol which distills over. Cool, rinse the phenol out of the side tube, dissolve the residue in the distilling bulb in water, filter, if necessary, and precipitate the salicylic acid from the filtrate with concentrated hydrochloric acid. Recrystallize from water, using a little bone-black, if the acid is colored. Yield 5 to 10 grams.

The potassium phenolate reacts at 150° in the same manner as the sodium salt, but at 220° it gives the parahydroxybenzoate instead of the salicylate.

This synthesis is quite general in its application, and derivatives of phenol react in a manner similar to phenol itself.

Salicylic acid crystallizes in white needles which melt at 156°. The solution gives an intense violet color with ferric chloride, a reaction characteristic of all orthohydroxy acids of the benzene series. Salicylic acid is often used in articles of food on account of its antiseptic properties, and the reaction with ferric chloride is made use of in its detection.

74. Preparation of an α-Hydroxy Acid from an Aldehyde, through the Cyanhydrine.—Mandelic acid,  $C_6H_5C(OH)(H)-CO_2H$ (phenethylolic acid).

Literature.—Winckler: Ann., 18, 310; Spiegel: Ber., 14, 239; Engler, Wöhrle: *Ibid*, 20, 2202; Wallach: Ann., 193, 38; Louguinine u. Naquet: *Ibid*, 139, 299; Müller: Ber., 4, 980.

20 grams benzaldehyde.
13 grams potassium cyanide.
15.3 cc. hydrochloric acid (sp. gr. 1.19).

Put into a small flask 13 grams (1 mol.) of *pure* potassium cyanide, and 20 grams (1 mol.) of freshly distilled benzaldehyde. Place the flask in ice-water, and drop in slowly from a burette 7 grams (1 mol.) of hydrochloric acid. This will be 14.3 cc. of an acid of sp. gr. 1.20, or 15.3 cc. of an acid of sp. gr. 1.19. During the addition of the acid shake frequently, and allow the mixture to stand for one hour after all has been added. Then pour into 150 cc. of cold water. Separate the cyanhydrine from the solution, and wash twice with water (see **51**, p. 127). Transfer the nitrile to a porcelain dish, add 50 cc. of concentrated hydrochloric acid, and evaporate on a sand bath till crystals begin to separate on the upper surface of the liquid. Dissolve the residue in about 100 cc. of warm water, filter from any oil which remains, and extract the mandelic acid from the filtrate with ether.

In extracting with ether, especially when, as in this case, the substance to be extracted is easily soluble in water, the solution should be as concentrated as possible. It is also an advantage, in many cases, to add salt or ammonium sulphate to the solution which is to be extracted. This lessens the solubility of the ether in the solution and also of the water in the ether. In extracting, put the solution to be extracted into a separatory funnel, which should be chosen of such size as to be nearly filled. Add, according to the ease with which the substance is extracted from the solution and according to the volume of the latter, 10-50 cc. of ether. When a substance is easily extracted, use but little ether; if extracted with difficulty, a larger amount; and the extraction must, in such a case, be many times repeated. These rules follow from the law for the division of a substance between two immiscible solvents, which is, that the amounts retained in a unit volume of each have a fixed ratio, independently of the volume of each. The ratio is called the partition coefficient, and in the present case expresses the amount of substance contained in 100 cc. of the aqueous solution divided by the amount contained in 100 cc. of the ethereal solution.

Expressed mathematically, let

x_0 = amount of substance present.
x_1 = amount of substance retained by the water.
$x_0 - x_1$ = amount of substance retained by the ether.
k = division-coefficient.
l = amount of water.
m = amount of ether.
$\frac{x_0 - x_1}{m}$ = concentration of the ethereal solution.
$\frac{x_1}{l}$ = concentration of the aqueous solution.

Then by the definition

$$k = \frac{x_1}{l} \div \frac{x_0 - x_1}{m} \text{ or } x_1 = kl\frac{x_0 - x_1}{m}$$

$$\text{or, } x_1 = x_0\frac{kl}{m + kl}$$

$$\text{and } x_0 - x_1 = x_0\frac{m}{m + kl}.$$

An examination of the last expression, which gives the amount of substance removed by a single extraction, shows that if *k* is large, that is, if the substance is very soluble in water in proportion to its solubility in ether, the amount extracted increases rapidly with the amount of ether used, but that several extractions must be required. If *k* is small, however, an increase of *m*, or the amount of ether, has little effect on the value of the fraction and a few extractions with a small amount of ether will suffice.

In extracting, after adding the ether, the stop-cock of the funnel should be inserted and held firmly in place while the contents are shaken vigorously. Only when there is danger of forming an emulsion which will separate into layers with difficulty, should the agitation of the liquids be more gentle. After shaking, the funnel should be inverted, and the stop-cock opened for a moment to relieve any pressure due to vapor of ether. The funnel is then set upright and allowed to stand till the two layers separate. In case separation does not take place satisfactorily it may be necessary to add more ether, or a few drops of alcohol. In extreme cases, filtration on a plate, or through a tube containing some cotton, may be necessary. Occasionally an emulsion can be caused to clear by connecting the funnel with the pump and exhausting till the ether boils for a short time. When separation has taken place, the aqueous solution is drawn off into a flask. It is usually an advantage when the solution has been nearly removed, to give the funnel a slight rotary motion to collect the solution at the bottom, where it can be drawn off. The ether is then poured *from the top* of the funnel into a flask or distilling bulb, care being taken not to pour out any drops of the aqueous solution which may remain.

The end of the extraction may be determined by taking a little of the ethereal solution in a dry test-tube, and evaporating the ether quickly by immersion in a boiling water-bath, and finally inverting the tube to allow the vapor of ether to fall out.

In working with small quantities, extractions may sometimes be made with advantage in a test-tube and the ethereal solution drawn off with a small pipette, suction being applied to the latter through a rubber tube long enough for the eye to be brought into a position to see the liquid. It is an advantage to draw the pipette out to a capillary below. (See Fig. 23, p. 54.)

The ethereal solution of the mandelic acid should be distilled and the residue dried on the water-bath in a watch-glass or porcelain dish. The acid, which crystallizes on cooling, may be recrystallized from benzene. Yield 10 to 15 grams.

Mandelic acid crystallizes from water in large rhombic crystals, and from benzene in leaflets, which melt at 118°. 100 parts of water at 20° dissolve 15.97 parts of the acid.

As with all substances prepared by synthesis from inactive bodies it is inactive, but, as it contains an asymmetric carbon atom, it may be separated into two active forms. The separation may be effected by the crystallization of the cinchonine salt, or by the growth of *Penicilium Glaucum,* or *Saccharomyces ellipsoïdeus* in a solution of the ammonium salt. The former destroys the levo form, the latter the dextro form.

75. Preparation of an Ester by Condensation by Sodium Ethylate.—Acetoacetic ester, $CH_3COCH_2CO_2C_2H_5$. (3-Butanonic ethyl ester.)

Literature.—Geuther: Jsb. d. chem., *1863,* 323; *1865,* 302; Frankland, Duppa: Ann., **135,** 220; **138,** 204; Wislicenus, Conrad: *Ibid,* **186,** 214; Michael: J. prakt. Chem. (N. F.), **37,** 473; Nef: Ann., **266,** 62; **270,** 331; Freer: Am. Chem. J., **13,** 310.

20 grams sodium.
200 grams acetic ester.

60 cc. glacial acetic acid.
60 cc. water.
100 cc. salt solution.

The acetic ester used for this preparation must be quite pure, as otherwise its action on sodium will be too violent. If a commercial ester of good quality is used, it will suffice to allow it to stand over night with one-fifth of its volume of granulated calcium chloride, and filter it through a dry filter. If, however, the ester is less pure or has an acid reaction, it must be shaken with a strong solution of sodium carbonate to remove acetic acid, with a 50 per cent. solution of calcium chloride to remove alcohol, dried with calcium chloride, distilled, and dried again as directed above.

Place in a 750 cc. flask 20 grams of sodium in the form of wire,[1] or cut in thin slices. Connect with a large upright condenser, and pour through the latter 200 grams of acetic ester. The heat of the reaction should cause the ester to boil, but the reaction should not be violent. When the action appears to slacken, or if it does not commence after a short time, place the flask on a water-bath and heat gently till the sodium has all dissolved. This will take one to five hours. To the slightly cooled solution add, with vigorous shaking, 60 cc. of glacial acetic acid diluted with an equal volume of water. The solution should now react faintly acid. Add 100 cc. of a cold saturated solution of common salt, shake, add enough water to dissolve any salt that separates, separate the upper layer containing the acetoacetic ester by means of a separatory funnel, and distil from a 500 c. distilling bulb, best of Ladenburg's form (Fig. 36), till the thermometer reaches 95°. This portion of the distillate contains acetic ester, and may be purified and used again. Transfer the residue in the distilling bulb at once to a 100 cc. distilling bulb fitted with a capillary tube, thermometer, and a second bulb connected to the side tube to collect the distillate (Fig. 34). Heat in an oil-bath[1] or in an air-bath consisting of a wrought iron crucible, so placed that the bulb does not touch it at any point. Distil under a pressure of 30-40 mm. till the thermometer reaches 80°, or to 90° under a pressure of 100 mm. Change the bulb used as a receiver and continue the distillation, cooling the receiver by running water over it. If the pressure remains constant,

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[1] For this and similar reactions the sodium is best pressed into the form of wire by means of a sodium press. The surface of the sodium mnst be cut clean, and it must not stand in the air before it is put into the press. After use, the press should be cleaned with alcohol and dried immediatelv. Finely divided sodium may also be easily prepared by putting the sodium in a small flask with some xylene and heating till the sodium melts. The flask is then stoppered and shaken vigorously for a short time. When cold the xylene may be decanted and, if necessary, the globules of sodium rinsed by decantation with dry ether or with low boiling petroleum ether.

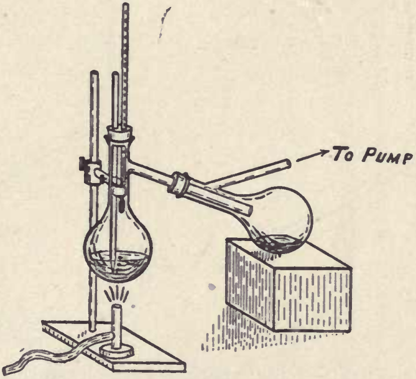

Fig. 34.

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[1] A bath of Wood's metal is especially convenient, if this is available. The first cost is considerably greater than that of oil but it is much cleaner and may be used almost indefinitely. For an oil-bath cotton-seed oil is suitable or a mineral oil with a very high flashing point.

after the boiling-point of the acetoacetic ester is reached, it will all pass over within an interval of a few degrees. The ester obtained by the first distillation should be fractioned once or twice under diminished pressure, and the ester finally obtained should boil within an interval of 2° to 3°, if the pressure is constant. Yield 45 to 50 grams.

The ester may also be distilled under ordinary pressure, but the yield is much less.

The success of this preparation depends very greatly on rapid work. If sodium in the form of wire is used, the whole preparation should be completed in three or four hours. If the preparation is interrupted at any point, and especially if allowed to stand over night, the yield is greatly diminished.

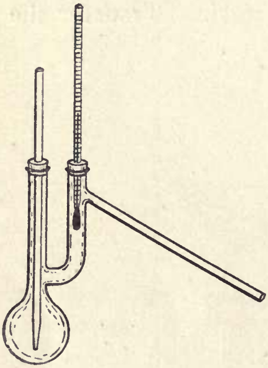


Fig. 35.

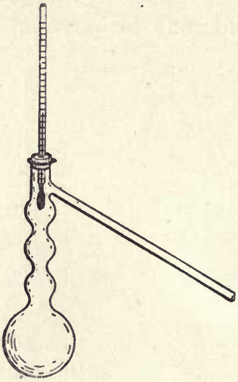


Fig. 36.

For the second distillation under diminished pressure a Claisen distilling bulb (Fig. 35) can be used with advantage. In all such distillations the temperature of the oil, metal- or air-bath should rise very slowly, and an oil-bath should not be heated much hotter than the boiling-point of the substance distilled. The capillary tube is to start bubbles of vapor and prevent bumping. It is best made from a capillary tube 5-6 mm. outside diameter, and drawn out to a fine thread.

Many different forms of apparatus have been devised for distillation under diminished pressure (Brühl: Ber., **21**, 3339;

Lothar Meyer: *Ibid,* **20**, 1833; Fuchs: Z. anal. Chem., **29**, 591; Mabery: Am. Chem. J., **17**, 722), but for most cases which arise in ordinary practice, the simple apparatus of Fig. 34, if a stream of cold water is kept running over the receiving bulb, answers every purpose. A good "Bunsen" pump which will reduce the pressure quickly to 30 mm. or less, when the water is cold, is, of course, required. The author has found that of E. C. Chapman, large size, the most satisfactory.

For substances of very high boiling-point or which decompose easily a mechanical pump (Geryk's) which will reduce the pressure to 1 mm. or less is of very great advantage, as a further decrease in boiling-point of about 100° may be obtained in this way.

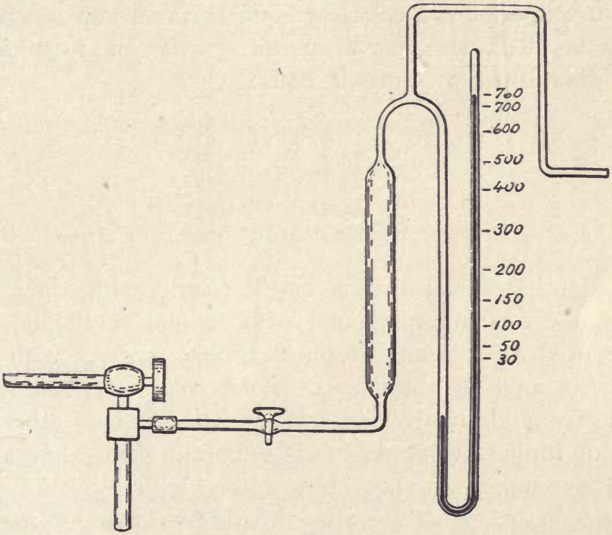


Fig. 37.

It is very convenient to have a manometer attached in such a manner that the pressure can always be known whenever the pump is used. That shown in Fig. 37 has been in use in the author's laboratory for some years, and has the advantage over the usual forms that the whole scale, from no pressure to that of the atmosphere, occupies a space of only about 18-20 cm., and further that the air in the closed end above the mercury acts as a cushion and there is no danger of breakage when the pressure is suddenly released. It is an advantage to have a portion of the bend at A, of capillary tubing 1 mm. or less in diameter.

The manometer is calibrated after it is put in position by comparison with the manometer of the usual form for low pressures, both being connected with the same receptacle, which is exhausted by the pump. For higher pressures it is calibrated by connecting with a small tube standing perpendicularly in a dish of mercury, subtracting the height of mercury in the tube from the height of the barometer for the day.

Acetoacetic ester is a colorless liquid with an unpleasant odor. It boils at 181°, and has a specific gravity of 1.030 at 15°. Under diminished pressure it boils:

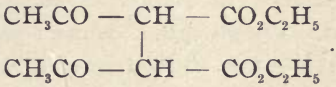
Under	12.5	mm.	at	71°.
"	18.0	"	"	79°.
"	29.0	"	"	88°.
"	59.0	"	"	97°.
"	80.0	"	"	100°.

It is slightly soluble in water and is volatile with water vapor. It gives a crystalline compound with sodium bisulphite, which may be used as a means of purification. It gives with ferric chloride, in aqueous solutions, a violet color—characteristic of ortho hydroxy derivatives of benzoic acid, and of other compounds of similar structure. It is soluble in cold dilute alkalies without decomposition, but on warming with alcoholic potash it is decomposed, chiefly with formation of two molecules of acetic acid and alcohol (acid decomposition). Boiling it with dilute acids or alkalies decomposes it mainly with the formation of acetone, carbon dioxide, and alcohol (ketonic decomposition). For the use of acetoacetic ester in syntheses, see p. 111.

On heating by itself, it decomposes with the formation of dehydracetic acid, $C_8H_8O_4$. This can be recovered from the residues after distilling off the acetoacetic ester, by boiling them with sodium carbonate and bone-black and crystallizing the sodium salt, after filtration. The latter is then decomposed with dilute sulphuric acid. The acid crystallizes in needles which melt at 109°. (Feist: Ann., 257, 253.)

By condensation of acetoacetic ester with aldehyde ammonia, a pyridine derivative is formed, with aniline a chinoline derivative, with phenyl hydrazine a pyrazolone compound, and with amidines pyrimidine compounds.

76. **Condensation of Acetoacetic Ester with Itself.**—Diacetyl succinic ester,



$$\begin{array}{l} CH_3CO - CH - CO_2C_2H_5 \\ \qquad\qquad\quad | \\ CH_3CO - CH - CO_2C_2H_5 \end{array}.$$

Literature.—Rugheimer: Ber., 7, 892; Harrow: Ann., 201, 144; Nef: *Ibid*, 266, 88; Knorr: Ber., 22, 170, 2100; Paal: *Ibid*, 18, 58, 2251.

150 cc. dry ether.
4 grams sodium.
20 grams acetoacetic ester.
20 grams iodine.
100 cc. ether.

Prepare some pure, dry ether as follows:[1] Fill a half liter Ladenburg distilling bulb (see 75, p. 172) one-fourth full with granular calcium chloride. Place in the bulb an inverted test-tube of such size and length as to reach just to the bottom of the neck and nearly close it, when resting on the bottom of the bulb. Fill the neck nearly to the side tube with granular calcium chloride, and then fill the bulb nearly to the neck with ordinary ether. Stopper the bulb and allow it to stand over night. Then distil on a water-bath, using a thermometer, and collecting the ether in a dry bottle. Change the receiver as soon as the thermometer rises 0.2° above the boiling-point of pure ether. The ether dried in this way will answer for this preparation. For a perfectly anhydrous ether some sodium wire must be pressed into it, and the ether distilled after standing for a day. See, however, pp. 82 and 74.

Ether should be kept in bottles with a smooth neck, and closed with a tightly fitting cork, not with a glass or rubber stopper. The stock of ether should be kept, as far as possible, in bottles which are filled full, as the loss is chiefly due to the expansion and contraction of the air above the ether, which always carries with it some of the vapor. The same is true of other volatile liquids.

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[1] Method suggested by Dr. H. H. Ballard.

Place in a 300 cc. flask about 150 cc. of dry ether, weigh carefully, and press into the flask about four grams of sodium wire, taking care, of course, that there is no appreciable loss of ether by evaporation. Weigh again, connect with an upright condenser, and for each gram of sodium add five grams of acetoacetic ester. Shake occasionally till the sodium is all dissolved, which will take from one to two hours. When an evolution of hydrogen is no longer observed, after shaking, add in small portions with shaking, a solution of about 20 grams of finely powdered iodine in dry ether. Continue the addition only so long as the color of the iodine disappears immediately after each addition. Filter from the sodium iodide, distil the ether, and crystallize the residue of diacetylsuccinic ester from glacial acetic acid.

Diacetylsuccinic ester crystallizes in needles, or in monoclinic plates, which melt at 88°.

If saponified by strong caustic soda at ordinary temperatures, the free acid can be obtained. If saponified by a 3 per cent. solution of caustic soda, in exactly equivalent amounts, however, acetonylacetone, alcohol, and carbon dioxide are formed.

77. Synthesis of an Acid by Condensation of Acetoacetic Ester with a Halogen Compound.—Hydrocinnamic acid,

$$C_6H_5CH_2CH_2CO_2H,$$

(Phen-3-propanoic acid).[1]

Literature.—Alexejew, Erlenmeyer: Ann., 121, 375; 137, 327; Gabriel, Zimmermann: Ber., 13, 1680; Fittig, Kiesow: Ann., 156, 249; Sesemann: Ber., 6, 1086; 10, 758; Conrad, Hodgkinson: Ann., 193, 300; Conrad: *Ibid,* 204, 136; Conrad, Bischoff: *Ibid,* 204, 180; Fittig, Christ: *Ibid,* 268, 122; For benzyl acetone, Ehrlich: *Ibid,* 187, 11; Jackson: Ber., 14, 890; Harries, Eschenbach: *Ibid,* 29, 383.

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[1] This acid is called, in the Third Edition of Beilstein, phenäthylsäure, but that name does not agree with the principles of nomenclature proposed by the Geneva Congress and Beilstein uses the same name elsewhere for *a*-toluic acid, $C_6H_5CH_2CO_2H$.

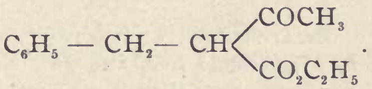
2.3 grams sodium.
35 cc. absolute alcohol.

13 grams acetoacetic ester.
12.6 grams benzyl chloride.

15 grams (about) benzyl acetoacetic ester.
30 cc. alcohol.
10 grams sodium hydroxide.
30 cc. water.

40 cc. hydrochloric acid (sp. gr. 1.11).

Put 2.3 grams (1 mol.) of sodium in a 100 cc. flask. Add 35 cc. of absolute alcohol, connect with an upright condenser, and heat on a water-bath till the sodium is dissolved. Cool, add 13 grams (1 mol.) of acetoacetic ester, which on shaking will cause the sodium ethylate, which has separated, to dissolve. Add 12.6 grams (1 mol.) of benzyl chloride, and heat on the water-bath with an upright condenser for two hours. The solution should now react neutral when a piece of dry reddened litmus paper is dipped in it and afterwards moistened. Cool, filter on a dry filter with the pump, and wash twice with a little alcohol. Distil the solution under ordinary pressure till the thermometer reaches 110°, and then under diminished pressure, using an oil- or metal-bath. The Claisen distilling bulb may be used with advantage (see 75, p. 172). The portion boiling at 160°-170° under a pressure of 12 mm., or 180°-190° under a pressure of 100 mm., will be nearly pure benzyl acetoacetic ester.



$$C_6H_5 - CH_2 - CH\left\langle\begin{matrix}COCH_3\\CO_2C_2H_5\end{matrix}\right. .$$

A small portion, which boils at 70° higher, consists of dibenzyl acetoacetic ester; 12-15 grams of the monobenzyl acetoacetic ester should be obtained.

Put the benzyl acetoacetic ester in a 200 cc. flask, add 30 cc. of alcohol, and 10 grams of sodium hydroxide dissolved in 30 cc. of water. Boil with an upright condenser for an hour. Cool, dilute with about 50 cc. of water, and extract twice with 10-20 cc. of ether. Distil off the ether, dry the ketone which remains *in vacuo* over sulphuric acid, and distil; or the ethereal solution may be dried with ignited potassium carbonate before the ether is distilled away.

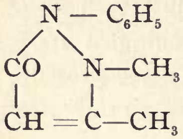
Evaporate the alkaline solution to about 20 cc. and add 40 cc. of hydrochloric acid (sp. gr. 1.11). The hydrocinnamic acid usually separates as an oil, at first, but will solidify on standing in a cool place for some time. Filter, and recrystallize from hot water, reserving a very small crystal to cause the solidification of the acid, in case it separates again as an oil.

The yield of the ketone and of the acid is about 3 grams each, but better yields may be obtained by working with larger quantities.

Benzyl acetone (1, 3-butylonephen $C_6H_5CH_2CH_2COCH_3$) is a liquid which boils at 235°-236°, and has a specific gravity of 0.989 at $\frac{23.5^\circ}{17.5^\circ}$.

Hydrocinnamic acid crystallizes in long colorless needles, which melt at 49°. It boils at 280°. It is easily soluble in boiling water, and in alcohol and ether. It is volatile in water vapor. It dissolves in 168 parts of water at 20°.

78. Preparation of a Pyrazolone Derivative.—Antipyrine,



1-Phenyl-2,3-dimethyl-pyrazolone.

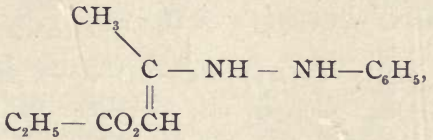
Literature.—Knorr: Ber., 16, 2597; 17, 549, 2037; 28, 706; Ann., 238, 137; 279, 188; 293, 1; Marckwald: *Ibid,* 286, 350; Nef: *Ibid,* 266, 131; 287, 353; Bender: Ber., 20, 2747; Patents, Knorr: *Ibid,* 17, R, 149; Meister, Lucius, and Brüning: *Ibid,* 18, R, 725; 20, R, 609; 27, R, 282.

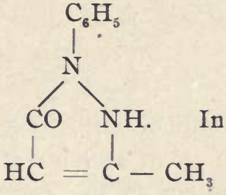
13 grams acetoacetic ester.
10 grams phenyl hydrazine.

10 grams 1-phenyl-3-methylpyrazolone.
10 grams methyl iodide.
10 grams methyl alcohol.

Put in a flask 13 grams of acetoacetic ester, add 10 grams of phenyl hydrazine, and heat on the water-bath for two hours, or till a drop of the mixture becomes perfectly solid on treating with a little ether on a watch-glass. Pour the warm mass, with stirring, into a small amount of ether, filter, wash with ether, and dry.

The acetoacetic ester and phenyl hydrazine condense at first with the formation of a hydrazide,

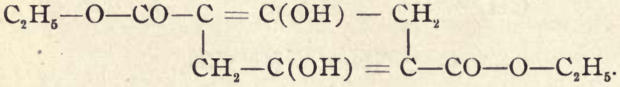


and this, on heating, condenses, with loss of alcohol, to 1-phenyl. 3-methylpyrazolone,  In working with larger amounts it may be desirable to separate the water formed by the first condensation as Knorr suggests, but the directions given are satisfactory for small amounts. The phenylmethylpyrazolone melts at 127°, is almost insoluble in cold water, ether and ligroïn, more easily soluble in hot water, and very easily soluble in alcohol. It dissolves both in acids and alkalies.

Put in a thick walled tube 10 grams of the phenylpyrazolone, 10 grams of methyl iodide, and 10 grams of methyl alcohol. Seal carefully, (see p. 156), and heat in a bomb oven, or in an iron tube (to guard against explosion) in a water-bath for two to three hours. Cool, open the capillary by softening in a flame, cut off the end, transfer the contents of the tube to a beaker, add a small amount of a solution of sulphur dioxide, and some water, boil to expel the alcohol, cool, add sodium hydroxide in slight excess, and extract several times with a small amount of chloroform. Distil off the chloroform, and crystallize the antipyrine from toluene. The yields are nearly quantitative, except for the loss in manipulations.

Antipyrine crystallizes in leaflets, which melt at 116°. It is easily soluble in water, alcohol, benzene, and chloroform, difficultly soluble in ether and ligroïn. The aqueous solution is colored red by ferric chloride. Dilute solutions give a bluish green color with nitrous acid.

79. Succinylosuccinic Ester.—



$$\begin{array}{lllll} C_2H_5{-}O{-}CO{-}C & = C(OH) - & CH_2 & & \\ \quad\quad\quad\quad\quad\ | & & | & & \\ \quad\quad\quad\quad\ CH_2{-}C(OH) & = & C{-}CO{-}O{-}C_2H_5. & & \end{array}$$

Literature.—Fehling: Ann., 49, 186; Herrmann: *Ibid,* 211, 306; Duisberg: Ber., 16, 133; Wedel: Ann., 219, 94; Baeyer: Ber., 19, 432; Mewes: Ann., 245, 74; Baeyer u. Noyes: Ber., 22, 2168; Pinner: *Ibid,* 22, 2623; Piutti: Gas. chim. ital., 22, 167.

50 grams succinic ester.
13.5 grams sodium.
2 cc. absolute alcohol.

Place in a 100 cc. round-bottomed flask 50 grams of succinic ester (see p. 152) and 2 cc. of absolute alcohol. Press into the flask 13.5 grams of sodium in the form of wire. (In such cases it is desirable to know how much sodium will be left in the press when the piston is forced to the bottom and allowance should be made for this. The press must be cleaned with alcohol and dried immediately after use. Instead of sodium wire finely divided sodium prepared as directed on p. 170 may be used.) During the addition of the sodium have a dish of cold water at hand, and cool the flask by immersion in this, if the reaction becomes violent. The flask should always be allowed to grow warm, but should not become so hot as to melt the sodium. When the sodium has all been added, and the reaction has progressed far enough so that the mixture no longer tends to grow hot, connect the flask with an upright condenser and heat on a water-bath for two hours. Stopper the flask and allow it to cool. The mixture can be left at this point over night without harm, perhaps with advantage. The yield can be increased by longer heating or longer standing, but the time taken is usually worth more than the material saved. The contents of the flask should, at the end of the time, be converted into a dry, solid mass.

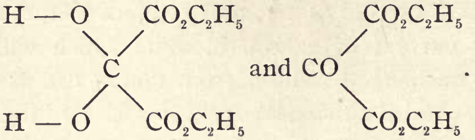
Put into a 500 cc. beaker 200 cc. of water and 150 cc. of dilute sulphuric acid (25 per cent., sp. gr. 1.18). Set the beaker in a large dish of cold water, and conduct to the surface of the acid a slow current of carbon dioxide, which will prevent the particles of unchanged sodium from taking fire as they dissolve in the acid. Add the material from the flask to the acid in small portions with vigorous stirring. It is frequently necessary to break the flask to get the sodium salt, but the latter should not be exposed to the air long before it is thrown into the acid.

The crude succinylosuccinic ester which separates is filtered off on a plate, and washed with cold water. The crude ester, after sucking as dry as possible, is then crystallized from hot alcohol. For this purpose put in a 500 cc. flask about 300 cc. of alcohol and add the ester only in such quantity that it dissolves quite readily on boiling the alcohol on a water-bath. Filter hot and very quickly on a plate, transfer the filtrate to a clean flask and cool rapidly under the tap till the ester has crystallized. Filter on another plate with a clean filter. Transfer the filtrate to the first flask, add more of the ester, boil, filter, crystallize and collect the crystals on top of the first lot. Repeat till all of the ester has been crystallized, then wash the crystals once with pure alcohol and repeatedly with dilute alcohol.

Succinylosuccinic ester forms yellowish or greenish crystals which melt at 127°. It is almost insoluble in cold water, slightly soluble in hot water, and difficultly soluble in cold alcohol. The pure alcoholic solution has a beautiful blue fluorescence, and is colored onion-red by ferric chloride. The ester dissolves in dilute caustic soda, and is saponified with formation of the products of both acid and ketonic decomposition by allowing the solution to stand (Herrmann: Ann., 211, 322). A clean ketonic decomposition with the formation of diketohexamethylene (cyclohexanedione 1.4) can be obtained by boiling with dilute sulphuric acid. (Baeyer: Ann., 278, 91.)

By suspending in carbon disulphide and treating with the calculated amount of bromine, it is converted quantitatively into dihydroxyterephthalic ester.

80. Preparation of Ethyl Dihydroxymalonate and Ethyl Oxomalonate.—(Ethyl ester of mesoxalic acid),

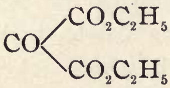


Literature.—Curtiss: Am. Chem. J., 35, 477; Curtiss and Spencer: J. Am. Chem. Soc., 31, 1054; Conrad, Brückner: Ber., 24, 3000; Anschütz, Parlato: Ber., 25, 3615; Color of organic compounds, Curtiss: J. Am. Chem. Soc., 32, 795.

35 grams malonic ester.

35 grams oxides of nitrogen (NO and NO_2).

Put 35 grams of malonic ester (see p. 136) in a 100 cc. flask and cool it to —13° with ice and salt or ice and commercial hydrochloric acid. Pass into the weighed flask the oxides of nitrogen prepared by dropping nitric acid (sp. gr. 1.42) slowly upon 100 grams of arsenic trioxide while the mixture is gently warmed. Pass the gases through an empty flask or wash bottle to condense moisture. Continue the passage of the gas till the flask gains 35 grams in weight. Pack the flask in the freezing mixture and allow it to stand over night, closing it with a cork stopper bearing a tube closed with a Bunsen valve.[1] Then allow the ice to melt and the mixture to come to room temperature, allowing it to stand for 24 hours longer. Note the loss in weight. The color should now be dark green. Aspirate or blow air through the liquid for 10-15 minutes to remove the excess of oxides of nitrogen. Distil the residue under diminished pressure, using a Raikoff receiver, (Chem. Ztg., *1888*, 693), collecting the distillate in three portions, the first containing water, acetic acid and ester, the second, colorless dihydroxy malonic ester and the third, to be collected when the distillate becomes green, oxomalonic ester,



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[1] A piece of soft rubber tubing closed at the end with a glass rod and having two short, longitudinal slits cut in its walls.

To obtain the dihydroxymalonic ester from the green oxomalonic ester allow it to stand in the air for some hours with occasional stirring. Water will be absorbed and the substance will pass over into the colorless, crystalline hydroxy compound. When the transformation appears to be complete filter on a plate (p. 120) and suck as dry as possible. Stop the pump, moisten the crystals with a little carbon disulphide and suck off again. Repeat twice and then recrystallize from a mixture of equal parts of ligroïn and benzene. Dihydroxymalonic ester crystallizes in colorless plates which melt at 57°. Yield 28 to 30 grams.

The anhydrous keto ester may be prepared by mixing the dihydroxy compound with twice its weight of phosphorus pentoxide (about 3 mols.) in a large distilling bulb and distilling under diminished pressure after standing for twenty-four hours. It boils at 115° under a pressure of 29 mm.

Dihydroxymalonic ester furnishes an illustration of the fact that when a carbon atom is combined with one or two negative groups it may retain two hydroxyl groups in combination.[1] To show the dissociation of the compound put 0.25 gram in a test-tube and warm very gently till it melts. Notice that the liquid is colorless. Raise the temperature to 90°-100°. As the compound dissociates and the water distils to the upper part of the tube the thick oil which remains gradually becomes greenish in color, the three carbonyl groups acting as a chromophore group. The saturation of the central carbonyl group by the addition of water, hydrochloric acid or other compounds destroys the chromophore grouping. Cork the tube and allow it to stand and notice the gradual recombination of the oxomalonic ester and water to form the crystalline, colorless dihydroxy compound.

[1] Another illustration is chloral hydrate. In crystallized oxalic acid *three* hydroxyl groups are probably combined with a single carbon atom.

Chapter X

CARBOHYDRATES

The most important carbohydrates are sucrose, maltose, lactose, glucose and fructose, of the sugars, and dextrin, starch and cellulose of the more complex compounds of the group.

Sucrose or cane sugar is prepared from the juice of the sugar cane, the sugar-beet or from the sap of the maple. It crystallizes well from water and from alcohol and is easily obtained in a high dgree of purity. Lactose, or milk-sugar is obtained from the whey which remains after separating casein from milk in the manufacture of cheese. Maltose is formed, together with dextrin, by the action of the enzyme, diastase, of malt, on starch. Glucose is prepared, commercially, by the hydrolysis of starch with dilute acids and crystallized *d*-glucose is now an article of commerce. In the laboratory it is more easily obtained from the mixture of *d*-glucose and *d'*-fructose obtained by the hydrolysis of sucrose. (Soxhlet: J. prakt. Chem. [2], **21**, 244; Müller: *Ibid.* [2], **26**, 83; Otto: *Ibid,* [2], **26**, 91.) *d'*-Fructose may be prepared from the same mixture by first combining it with calcium to form a difficulty soluble compound (Dubrunfant: Bull. soc. chim., **13**, 350. See also Girard: Bull. soc. chim., **33**, 154).

Starch is prepared, chiefly by mechanical processes, from corn or maize, potatoes, wheat or rice, the first two being the chief commercial sources. It cannot be crystallized and the molecular weight is not known.

Dextrin is a hydrolytic product, intermediate between starch and maltose or *d*-glucose, formed by the action of diastase or of acids on starch. Several different forms, which are fairly distinct in their properties, have been prepared. All forms are insoluble in alcohol and easily soluble in water. (See Lintner and Düll: Ber., **26**, 2543, and Brown and Millar: J. Chem. Soc., **75**, 288.)

Cellulose is prepared by the successive treatment of cotton or other natural fibers with ether, alcohol, water, alkalies and dilute hydrochloric and hydrofluoric acids to remove all substance soluble in these solvents. Cross, Bevan and Beadle distinguish three forms. (Ber., 26, 2524; J. Chem. Soc., 67, 438.) Cellulose is dissolved by Schweitzer's reagent (p. 189), but is probably changed, chemically, by the process (Bumcke and Wolfenstein: Ber., 32, 2494).

The most important quantitative methods for the determination of sugars are the determination of the specific gravity of solutions, the determination of the rotation of polarized light with the polarimeter or saccharimeter and the determination of reducing sugars with Fehling's solution, (see below).

The most important reactions which have established the structure of some of the sugars are the preparation of pentacetyl glucose (Erwig and Königs: Ber., 22, 1464), the preparation of the cyanhydrine and of glucoheptonic acid (Kiliani: Ber., 19, 768; Fischer: Ann., 270, 71 and 84) and the reduction of the latter to normal heptylic acid (Kiliani: Ber., 19, 1130; E. Fischer, Tafel: Ber., 21, 2175), the preparation of glucosazone from both *d*- glucose and *d'*-fructose, (p. 191) and the relation established between the molecular rotation of the α and β forms of the sugars (Hudson: J. Am. Ch. Soc., 31, 66).

The formation of furfural from pentoses furnishes an important method for the quantitative determination of pentosans (p. 190).

The formation of levulinic acid from glucose (p. 192) and of alcohol from glucose or fructose are illustrations of complex rearrangements which may be produced in carbohydrates by dilute acids or enzymes.

81. Fehling's Solution. Its Effect on Some of the Sugars. Inversion of Sucrose.

Literature.—History of Fehling's solution, Herstein: J. Am. Ch. Soc., 32, 779; Use for the quantitative determination of *d*-glucose and of invert sugar, alone and in the presence of sucrose, Munson and Walker: J. Am. Ch. Soc., 28, 663; Quantitative determination of lactose and maltose, Walker: J. Am. Ch. Soc., 29, 541; Chemical action of Fehling's solution, Nef: Ann., 357, 214; Theory of the failure of copper to precipitate in an alkaline solution, Meyer and Jacobson: Lehrb. Org. Chem., 1 Aufl., Vol. 1, p. 804; Hollemann: Lehrb., org. Chem., 2te Aufl., p. 205; See also Staedeler and Krause: Jahresb., 1854, 746; Hofmeister: Ann., 189, 27.

3.4639 grams pure crystallized copper sulphate.
Water to make 50 cc.

17.3 grams sodium potassium tartrate (Rochelle salt).
5.0 grams sodium hydroxide.
Water to make 50 cc.

For the quantitative determination of reducing sugars Fehling's solution must be prepared accurately in accordance with the directions given above, the quantities taken for the preparation being usually ten times as great. The alkaline solution of Rochelle salt changes slowly on standing, however, and it is not advisable to use for work intended to be accurate a solution which has stood for more than a few weeks. For the qualitative purposes indicated here dissolve 3.5 grams of copper sulphate in 50 cc. of water, and prepare a separate solution by dissolving 17 grams of Rochelle salt in 15 cc. of warm water, adding 15 cc. of a solution of sodium hydroxide (3 cc. = 1 gram), cooling and diluting to 50 cc. Equal volumes of the two solutions may be mixed and the mixture used for qualitative purposes at any time within a few hours.

Prepare one per cent. solutions of sucrose, maltose, glucose and lactose by dissolving 0.1 gram of each in 10 cc. of water. Also prepare a solution of invert sugar (mixture of *d*-glucose and *d'*-fructose) by adding a drop of concentrated hydrochloric acid to 5 cc. of the one per cent. solution of sucrose, boiling for about one minute, cooling and adding 5 or 6 drops of a 10 per cent. solution of sodium hydroxide.

Put 5 cc. of the mixed Fehling's solution in a test-tube, add 5 cc. of water, and one drop of the one per cent. solution of glucose. Boil for one minute. If no precipitate of red cuprous oxide appears, add more of the sugar solution and boil again. Repeat the experiment with each of the solutions prepared. Also add an excess of the glucose solution to a small portion of the diluted Fehling solution and note the complete discharge of the blue color after boiling and standing.

82. Preparation of a Sugar by the Action of an Enzyme.—Maltose and Dextrin.

Literature.—Soxhlet: J. prakt. Chem., [2], 21, 276; Herzfeld: Ann., 220, 211; Ber., 12, 2120; Noyes: J. Am. Chem. Soc., 26, 274; Hydrolysis of starch by acids, Rolfe and Defren: J. Am. Ch. Soc., 18, 869.

100 grams starch.
500 cc. hot water.

10 grams malt.
30 cc. water.

Rub up 100 grams of starch with a small amount of water in a mortar, using just enough water to form a uniform, rather thick cream, which can be poured into a liter flask. Add 500 cc. of boiling water and, if necessary, boil for a few minutes to form a clear, nearly transparent paste. Cool to 60° and add 10 grams of malt which has been digested for a short time with tepid water. Maintain the temperature at 60° for 20 minutes by immersion in a water-bath of that temperature. Filter on a plain or plaited filter. Put the solution in a one liter distilling bulb, connect another bulb to the side tube (Fig. 34, p. 171) and distil under diminished pressure till a thick syrup of maltose and dextrin remains. Add 300-400 cc. of alcohol (sp. gr. 0.83) and pour off the solution of maltose from the precipitated dextrin. The dextrin may be purified by dissolving in a small amount of water and precipitating again with alcohol of the same strength and repeating till the solution of dextrin gives only a trifling reaction for maltose with Fehling's solution (p. 185). After the last precipitation the dextrin, which precipitates as a gummy mass may be rendered comparatively dry and pulverulent by digesting it for some time with strong alcohol.

Unite the first and second alcoholic mother-liquors, containing the maltose, distil away the alcohol and water under diminished pressure till a thick syrup remains. Dissolve this in 200-300 cc. of hot, 90 per cent. alcohol, filter, if necessary, and allow the maltose to crystallize from the filtrate, adding a very little finely powdered maltose to the cold solution to start the crystallization.

Maltose crystallizes in fine needles, with one molecule of water, which is lost at 135°. Its specific rotation calculated for anhydrous maltose is $(\alpha)^{20^\circ}_D = 137.04^\circ$. It reduces Fehling's solution but the copper factor is much smaller than for glucose.

The dextrin prepared as directed is not very definite in its properties. It has a specific rotation of somewhat more than 200°, and does not reduce Fehling's solution.

83. Determination of the Specific Rotation of Sucrose and of Invert Sugar.

Literature.—Wiley: Principles of agricultural analysis, Vol. 3, p. 105; Bulletins of U. S. Department of agriculture giving methods of analysis adopted by the Association of Official Agricultural Chemists; Effect of hydrochloric acid on the rotatory power of invert sugar, Tolman: J. Am. Chem. Soc., 24, 515; Analysis of sugar mixtures, Browne: J. Am. Chem. Soc., 28, 439; Specific rotation, Noyes: Org. Chem., p. 47; Effect of temperature on the specific rotation of sucrose, Wiley: J. Am. Chem. Soc., 21, 568; Methods of the International Commission on Sugar Analysis: J. Am. Chem. Soc., 23, 59; Inversion by acid mercuric nitrate, Cochran: J. Am. Chem. Soc., 29, 555.

Weigh 20 grams of the best granulated sugar or of powdered rock candy in a porcelain dish or in a sugar scoop to an accuracy of 5 mg. Put a funnel in the mouth of a 100 cc. graduated flask; rinse the sugar into the flask, make up the volume to about 90 cc. and shake till the sugar is completely dissolved, make the solution up to exactly 100 cc., mix thoroughly and filter on a dry filter, if the solution is not absolutely clear, rejecting the first 20 cc. of the filtrate (why?) and collecting the remainder in a dry flask. Fill a 1 or 2 decimeter polarimeter tube with the solution, determine the angle of rotation with sodium light and calculate the specific rotation. The value found will usually be a little too low because the sugar is not quite pure.

Take exactly 50 cc. of the solution, add 5 cc. of concentrated hydrochloric acid and immerse the flask containing the mixture in a bath at 67° for 15 minutes, cool, transfer to a 100 cc. measuring flask, fill to the mark, mix thoroughly and determine the rotation and specific rotation for invert sugar as before. If a sugar flask graduated at 50 and 55 cc. is available, this may be used instead of following the directions given and the second readings may be taken in a tube 110 or 220 mm. long. *The temperature at which the readings for the invert sugar are taken must be noted carefully.*

On the basis of the results found explain Herzfeldt's formula for determining sucrose in the presence of other sugars not affected by acids under the conditions of inversion given. The formula is (Z. Rübenzucker-Ind., **40**, 194):

$$S = \frac{a - b}{141.85 + 0.05b - T/2}$$

S = Per cent. sucrose.
a = Direct reading.
b = Invert reading.
T = Temperature.

The readings a and b are for an instrument such that the normal weight of pure sugar (26. grams in 100 cc.) would give a reading of 100. The reading b, which is usually negative, is to be taken in the formula with its appropriate algebraic sign.

Why can white light be used with the ordinary saccharimeters having a quartz compensation system, while sodium light must be used for instruments reading with angular degrees? Can the quartz compensation instrument be properly used for the determination of specific rotation in general?

84. Schweitzers Reagent. Solution of Cellulose.

Literature.—Watts Chemical Dict., Vol. 1, p. 714; Erdmann: J. prakt. Chem., **76**, 385; Bumcke and Wolfenstein: Ber., **32**, 2494, 2502.

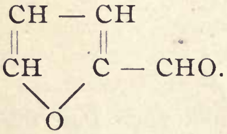
10 grams crystallized copper sulphate.
150 cc. water.
5 cc. ammonium chloride solution (10 per cent.).
Sodium hydroxide (10 per cent.).

30 cc. ammonium hydroxide (0.90).

Dissolve 10 grams of crystallized copper sulphate in 150 cc. of warm water, add 5 cc. of a solution of ammonium chloride (10 per cent.), cool thoroughly and add a ten per cent. solution of sodium hydroxide in excess. Wash the precipitated copper hydroxide at first by decantation and then thoroughly on a plate. Dissolve the precipitate in 30 cc. of ammonium hydroxide (sp. gr. 0.90) and filter on glass wool or asbestos. Dissolve some filter-paper or cotton in the reagent, filter and precipitate the cellulose with dilute hydrochloric or sulphuric acid.

The solution of cellulose in Schweitzer's reagent destroys the organized structure, of course, and the precipitate obtained with acids is amorphous. It is somewhat uncertain whether the chemical nature of the cellulose is changed by the process or not.

85. Preparation of Furfural from a Pentose.

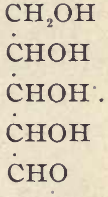


Literature.—Hill: Am. Chem. J., 3, 33; Stone: Ber., 24, 3019; Am. Chem. J., 13, 73, 348; Günther, de Chalmot and Tollens: Ber., 23, 3575; Stone and Tollens: Ann., 249, 227; Allen and Tollens: *Ibid*, 260, 291; Stone: J. Anal. Appl. Chem., 5, 421.

100 grams cobs of Indian corn.
500 cc. hydrochloric acid (sp. gr. 1.06).

Put in a liter distilling bulb 100 grams of coarsely powdered corn cobs (or wheat straw, or wheat bran, but the yield will be smaller), and 500 cc. of hydrochloric acid, of specific gravity 1.06 (140 cc. acid of sp. gr. 1.19, and 360 cc. of water). Fit in the mouth of the bulb a cork bearing a dropping funnel, and connect with a condenser. Heat to boiling,and distil slowly, at the rate of about 200 cc. in an hour, dropping in dilute hydrochloric acid (75 cc. acid sp. gr. 1.11, to 500 cc. of water), at such a rate as to keep the contents of the bulb constant in volume. Continue the distillation for three hours, or till 600-700 cc. have distilled. Add a drop of methyl orange, and nearly neutralize the distillate with a strong solution of caustic soda; add 150 grams of salt, and distil off about 200 cc. Add 60 grams of salt to the distillate, and extract with ether. Dry the solution with calcium chloride, distil off the ether, and distil the furfural which remains. Yield 11 to 12 grams.

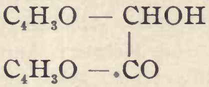
Certain gums contained in the materials used are hydrolyzed by the dilute acid, with the formation of a pentose,



$$\begin{array}{c} CH_2OH \\ CHOH \\ CHOH \\ CHOH \\ CHO \end{array}.$$

The pentose then condenses to furfural.

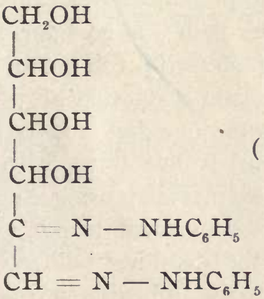
Furfural is a colorless oil, which boils at 161°, and has a specific gravity of 1.1636 at 13.5°. Its odor resembles that of benzaldehyde. By boiling with potassium cyanide, in dilute alcoholic solution, it is converted into furoïn,



$$\begin{array}{l} C_4H_3O - CHOH \\ \qquad\qquad | \\ C_4H_3O - CO \end{array}$$

, in the same manner in which benzaldehyde is converted into benzoïn (see 37, p. 97). It condenses easily with ammonia in aqueous solution to furfuramide, $(C_5H_4O)_3N_2$, which is difficultly soluble. It gives a hydrazone with phenyl hydrazine, and gives a red compound with aniline acetate. Filter-paper moistened with aniline acetate, furnishes a very sensitive qualitative test for furfural.

86. Preparation of an Osazone.—Glucosazone.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ C = N - NHC_6H_5 \\ | \\ CH = N - NHC_6H_5 \end{array}$$

(Dextrosazone, levulosazone).

Literature.—E. Fischer: Ber., 17, 580; Jaksch: Z. anal. Chem., 24, 478; Beythien: Ann., 255, 218.

2 grams glucose.
4 grams phenyl hydrazine.
10 cc. acetic acid (30 per cent.).
50 cc. water.

Dissolve 2 grams of glucose in 50 cc. of water, add a solution of 4 grams of phenyl hydrazine in 10 cc. of acetic acid, and heat on a water-bath for two hours. Cool, filter off the glucosazone and recrystallize it from 80 per cent. alcohol.

Glucosazone melts, when heated quickly, at 206°, and crystallizes in characteristic yellow needles. With diphenylhydrazine glucose gives an even more characteristic hydrazone. (Stahel: Ann., 258, 244.)

87. Preparation of Levulinic Acid by the Action of a Dilute Acid on a Carbohydrate, $CH_3COCH_2CH_2CO_2H$.

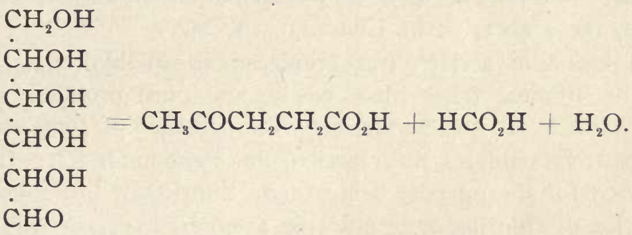
Literature.—Noeldecke: Ann., 149, 224, 228; Bente: Ber., 8, 416; Tollens and Kehrer: Ann., 175, 181; 206, 207; Conrad: Ber., 11, 2178; Wolff: Ann., 208, 105; Kent and Tollens: *Ibid*, 227, 229; Conrad and Guthzeit: Ber., 18, 442; 19, 2572; Neugebauer: Ann., 227, 99; Rischbieth: Ber., 20, 1773; Wehmer and Tollens: Ann., 243, 314; Seissl: *Ibid*, 249, 275; Fittig: Ber., 29, 2583.

100 grams sugar.
400 cc. water
100 cc. concentrated hydrochloric acid.

Put in a 750 cc. flask 100 grams of cane-sugar, 400 cc. of water, and 100 cc. of concentrated hydrochloric acid. Close the flask with a tube containing water as in the preparation of camphoric acid (see p. 122). Heat on a water-bath for 20 hours Filter on a plate, boil the residue of humus with 100 cc. of water and filter. To the combined filtrates add a solution of 35 grams of sodium hydroxide, and evaporate to about 100 cc. Filter again, if necessary, and extract four or five times with 50-75 cc. of ether, distilling the ethereal extract and using the same ether each time. For such cases it is convenient to put a dropping funnel through the stopper of the distilling bulb so that the ether may be introduced continuously and without removing the bulb from the water-bath. A funnel should be placed in the mouth of the dropping funnel to facilitate the pouring of the ether, and care must always be taken to avoid ignition of the latter.

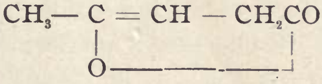
After distilling off the ether, transfer the residue to a smaller distilling bulb, and distil under diminished pressure, raising the temperature of the oil or air-bath slowly. Collect the portion boiling at 140°-160° under 15 mm., or at 160°-180° under 80-100 mm. Put this portion in a wide-mouthed, tightly stoppered bottle and allow to stand at 0° for some time, till it has solidified as far as possible. Pour off the liquid part, warm the residue gently till it melts, and allow it to crystallize slowly at ordinary temperatures. After draining off the liquid part the solid acid will be nearly pure. Yield 10-15 grams.

The reactions which take place are, first, the inversion of the cane-sugar to levulose and glucose, and then the decomposition of these into levulinic and formic acids and water.

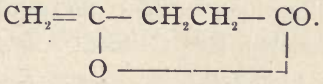


$$\begin{array}{l} CH_2OH \\ \dot{C}HOH \\ \dot{C}HOH \\ \dot{C}HOH \\ \dot{C}HOH \\ \dot{C}HO \end{array} = CH_3COCH_2CH_2CO_2H + HCO_2H + H_2O.$$

Levulinic acid melts at 33°, and boils with slight decomposition at 245°-246° under 760 mm. pressure, or 148°-149° under 15 mm. If heated for some time at its boiling-point, it is converted into a mixture of α- and β-angelica lactones,



and



It gives with phenylhydrazine a crystalline hydrazone, and is reduced to γ-hydroxyvaleric acid by sodium amalgam. On acidifying a solution of the sodium salt of this acid, valerolactone separates.

Chapter XI

HALOGEN COMPOUNDS

Chlorine and bromine derivatives of the hydrocarbons may be obtained by the direct action of the elements on the hydrocarbons. In the fatty acid series of hydrocarbons this method of preparation is of scarcely more than theoretical interest, partly because the hydrocarbons are difficult to obtain in pure condition, and partly because both primary and secondary halogen alkyls are formed, and frequently di- and tri-substitution products as well. If a complete replacement of the hydrogen by chlorine or bromine is desired, the addition of a small amount of iodine greatly facilitates the action. (For the chlorination of butane from petroleum, see Mabery: Am. Chem. J., 19, 247.)

In the aromatic series direct replacement of hydrogen by chlorine or bromine takes place easily, and pure products are readily obtained. In this series, also, the presence of some substances greatly facilitates the reaction, the compounds most frequently used for the purpose being ferric chloride or bromide.

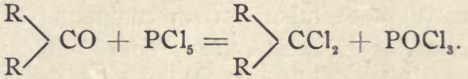
The action of chlorine or bromine on aromatic hydrocarbons in the cold and dark, but with the addition of ferric chloride or bromide, (or some powdered iron), causes a substitution of the hydrogen in the nucleus, and usually in the para or ortho position with reference to the side chain. In the sunlight, or with the boiling hydrocarbon, the substitution takes place in the side chain. (Beilstein and Geitner: Ann., 139, 331; Jackson: Am.Chem. J., 1, 94; 2, 1.)

The monohalogen derivatives of saturated hydrocarbons are usually most easily obtained from the corresponding alcohols by treatment with phosphorus trichloride, tribromide (or red phosphorus and bromine), or pentaiodide,

$$3ROH + PBr_3 = 3RBr + H_3PO_3.$$

$$5ROH + 5I + P = 5RI + H_3PO_4 + H_2O.$$

Dihalogen substitution products are often obtained from hydrocarbons of the ethylene series by direct addition, giving compounds in which the halogen atoms are combined with adjacent carbon atoms. They may also be obtained from ketones or aldehydes by treatment with phosphorus pentachloride or pentabromide, giving compounds in which the halogen atoms are combined with the same carbon atom.

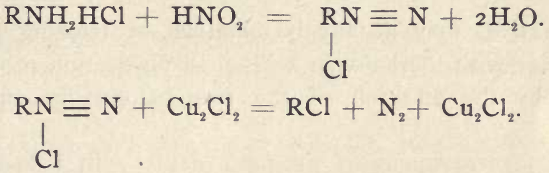


$$\begin{matrix}R\\ R\end{matrix}\!\!>CO + PCl_5 = \begin{matrix}R\\ R\end{matrix}\!\!>CCl_2 + POCl_3.$$

Monohalogen derivatives of the ethylene series may be prepared by treating di-halogen derivatives of the marsh gas series with alcoholic potash or soda.

$$C_nH_{2n}Br_2 + KOH = C_nH_{2n-1}Br + KBr + H_2O.$$

In the aromatic series halogen derivatives are often prepared from the amines by passing through the diazonium compounds (Sandmeyer's reaction).



$$RNH_2HCl + HNO_2 = \underset{\displaystyle Cl}{\underset{|}{RN}} \equiv N + 2H_2O.$$

$$\underset{\displaystyle Cl}{\underset{|}{RN}} \equiv N + Cu_2Cl_2 = RCl + N_2 + Cu_2Cl_2.$$

Finely divided metallic copper may be used in place of the cuprous chloride (Gattermann's reaction).

For iodine derivatives a very clean reaction can often be obtained by mixing such an acid diazonium solution as is described on pp. 201 and 131 or one containing somewhat more acid, with an excess of potassium iodide and warming the solution.

The action of hypochlorites, hypobromites, or hypoiodites upon some organic compounds causes a substitution of halogen atoms for hydrogen, a reaction which is of very great technical importance in the preparation of chloroform and iodoform. In the former case, when acetone is used, three hydrogen atoms in one of the methyl groups appear to be at first replaced by chlorine.

$$2CH_3 - CO - CH_3 + 3CaO_2Cl_2 = 2CCl_3COCH_3 + 3Ca(OH)_2.$$

The accumulation of negative atoms appears to render the trichloracetone unstable toward bases, and it decomposes in a manner which recalls the "acid decomposition" of β-ketonic acids (see 112).

$$2CCl_3COCH_3 + Ca(OH)_2 = 2CHCl_3 + Ca(CH_3CO_2)_2.$$

Most of the methods given for the preparation of halogen derivatives of hydrocarbons may also be used for the preparation of halogen derivatives of other carbon compounds.

Halogen derivatives of acids are prepared by treating the acid, or, in many cases, either the chloride or bromide of the acid, with the free halogen. Unless the temperature is unduly raised so as to cause secondary reactions, aliphatic acids give by this treatment only α derivatives. (Erlenmeyer: Ber., 14, 1318; Hell: *Ibid,* 14, 891; Auwers: *Ibid,* 24, 2209, 2233; Michael: J. prakt Chem. [2], 36, 92; Volhard: Ann., 242, 161.)

$$3C_nH_{2n+1}CO_2H + P + 11Br = 3C_nH_{2n}BrCOBr + HPO_3 + 5HBr.$$

β derivatives may usually be obtained by treating αβ unsaturated acids with the halogen acids. Bisubstitution products are obtained by the addition of the free halogen to unsaturated acids.

The direct treatment of aromatic acids with halogens gives chiefly meta compounds.

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88. Preparation of an Iodine Derivative of a Hydrocarbon from an Alcohol.—Methyl iodide, CH_3I.

Literature.—Dumas, Peligot: Ann., 13, 78; Rieth, Beilstein: *Ibid,* 126, 250; Walker: J. Chem. Soc., 61, 717.

3 grams red phosphorus.
9 grams methyl alcohol.
25 grams iodine.

Place in a 50 cc. distilling bulb 3 grams of red phosphorus, add 9 grams (11 cc.) of methyl alcohol, and then, in small portions, and with careful cooling 25 grams of iodine. Allow the mixture to stand in cold water for an hour and then distil from the water-bath, using a good condenser. Shake the distillate twice with an equal volume of water, separating with a separatory funnel (see **51**, p. 127), add once more an equal volume of water and, with frequent shaking, caustic soda till the methyl iodide is colorless. Separate again, transfering the iodide to a small distilling bulb, add some fused, powdered calcium chloride and distil again from the water-bath after about an hour, using a thermometer. Yield 20-25 grams.

Methyl iodide boils at 42.8°, and has a specific gravity of 2.2852 at 15°, or 2.2529 at 25°. On heating with fifteen parts of water at 100° it is converted into methyl alcohol and hydriodic acid.

Because of its low boiling-point and high molecular weight it escapes rapidly unless kept in small bottles tightly stoppered with cork stoppers, or, better, in sealed tubes. A globule of mercury is sometimes placed in the bottle to remove iodine. For the preparation of large quantities of ethyl or methyl iodide the method of Walker (*loc. cit.*) is to be recommended.

89. Preparation of a Bromine Derivative of a Hydrocarbon from an Alcohol with Sulphuric Acid and Potassium Bromide. —Ethyl bromide, C_2H_5Br.

Literature.—Serullas: Ann. chim. phys. [2], **34**, 99, (1827); Loewig: Ann., **3**, 288; Perkin: J. prakt. Chem., [2], **31**, 497; R. Schiff: Ber., **19**, 563; Riedel: *Ibid*, **24**, R. 105.

90 grams potassium bromide.
70 cc. water.

100 cc. alcohol.
100 cc. concentrated sulphuric acid.

10 cc. water.

Put 100 cc. of concentrated sulphuric acid in a flask, add slowly with constant shaking, but within two or three minutes, 100 cc. of alcohol. Cool thoroughly and pour the mixture into a 400 cc. distilling bulb or flask containing 90 grams of potassium bromide, and 70 cc. of water. Distil quite rapidly, heating on a wire gauze covered with a thin sheet of asbestos and using a good condenser, as long as ethyl bromide comes over. A little water should be placed in the receiver to absorb some hydrobromic acid, which is given off. Separate the ethyl bromide from the aqueous layer and add to it, with careful cooling, concentrated sulphuric acid till the acid separates below. This will remove any ether which has been formed. Separate again, wash twice with a small amount of water, put the bromide in a distilling bulb with some fused, powdered calcium chloride and distil, with a thermometer, after one or two hours. Yield 55 to 60 grams.

The reactions involved in the preparation are as follows.

$$C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl sulphuric acid}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 + KBr = \underset{\text{Ethyl potassium sulphate}}{C_2H_5KSO_4} + HBr$$

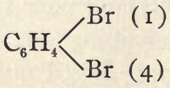
$$C_2H_5KSO_4 + HBr = C_2H_5Br + HKSO_4.$$

Ethyl bromide may also be prepared by the action of bromine on red phosphorus and alcohol, but the method here given is more satisfactory and gives a purer product, unless red phosphorus free from arsenic is available.

Ethyl bromide boils at 38.4°, and has a specific gravity of 1.476 at 15°. It must be kept in tightly corked, not glass stoppered bottles.

Ethyl bromide is sometimes used as an anaesthetic. For this use it must be entirely free from arsenic. Arsenic, if present, may be detected by burning the substance in a small spirit lamp, and drawing the products of combustion through a solution of caustic soda. The solution may then be tested for arsenic by means of hydrochloric acid and a concentrated solution of stannous chloride.

90. **Preparation of a Bromine Derivative of an Aromatic Hydrocarbon.**—Para-dibrombenzene.



$$C_6H_4\begin{cases}Br\ (1)\\ Br\ (4)\end{cases}$$

Literature.—Couper: Ann. chim. phys. [3], 52, 309, (1858); Riese: Ann., 164, 162; Jannasch: Ber., 10, 1355.

50 grams benzene (56.5 cc.).
210 grams bromine (67 cc.).
1 gram iron filings.

Put 50 grams of benzene in a dry, 200 cc. flask. Add 1 gram of iron filings or turnings, and close the mouth with a stopper bearing a dropping funnel which dips below the surface of the benzene, and an exit tube. Put in the dropping funnel, best out of doors, 67 cc. of bromine. Place the flask in a water-bath filled with cold water, and connect the exit tube with a tube opening just above the surface of water in a large bottle. Allow the bromine to flow slowly into the benzene. Toward the end, aid the reaction by heating the water-bath slowly to the boiling-point.

When the reaction is complete and no more vapors of bromine appear, distil from the flask or from a distilling bulb, collecting the portion boiling at 200°-230° by itself. Crystallize from a small amount of alcohol. Yield 50 to 60 grams of *p*-dibrombenzene.

Para-dibrombenzene crystallizes in white prisms or leaflets which melt at 89°, and boil at 219°.

91. Substitution of Chlorine in the Side Chain of an Aromatic Hydrocarbon.—Benzyl chloride, $C_6H_5CH_2Cl$.

Literature.—Cannizzaro: Ann., 96, 246; Beilstein, Geitner: *Ibid,* 139, 332; Lauth, Grimaux: *Ibid,* 143, 80; Schramm: Ber., 18, 608; Haase: *Ibid,* 26, 1053.

100 grams toluene.
100 grams manganese dioxide.
540 cc. commercial hydrochloric acid.

Put in a 200 cc. flask 100 grams (115 cc.) of toluene and connect it with an upright condenser. Place in the upper end of the condenser a tight stopper bearing two glass tubes, one passing just through the stopper and the other reaching nearly to the bottom of the flask. Connect the first tube with a tube opening just above the surface of water in a bottle. Or arrange one tube passing through the stopper beside the condenser, and connect the other with the top of the condenser, as in Fig. 38

Heat the toluene to boiling and pass in chlorine generated in a liter flask by the slow addition of 540 cc. of commercial hydrochloric acid to 100 grams of manganese dioxide, the mixture being warmed gently and the gas purified by passing it through a wash-bottle containing water, and then through one containing concentrated sulphuric acid. The operation must be carried out in clear daylight, or, if possible, in the direct sunlight.

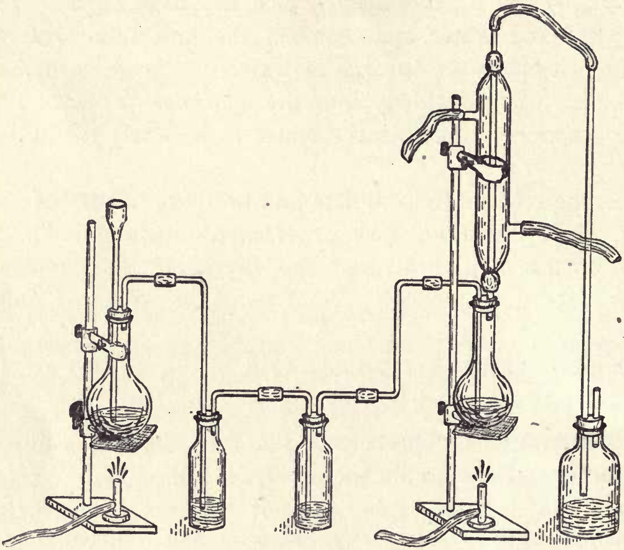
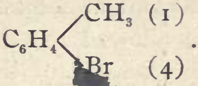


Fig. 38.

When the evolution of chlorine has ceased, submit the product in the flask to fractional distillation. The portion boiling below 150° consists chiefly of unchanged toluene and may be used for a new preparation. After fractioning two or three times the portion boiling at 176°-181° will consist of nearly pure benzyl chloride. The yield varies according to the brightness of sunlight in which the operation is conducted. In some cases the weight of benzyl chloride may equal that of the toluene used.

Benzyl chloride is a colorless liquid with an unpleasant odor. Its vapor attacks the eyes very strongly. It boils at 178° and has a specific gravity of 1.113 at 15°. By long boiling with water it is converted into benzyl alcohol. Oxidizing agents oxidize it to benzoic acid. The higher boiling portions contain some benzal chloride, $C_6H_5CHCl_2$, which boils at 203.5°.

92. Preparation of a Bromine Derivative of a Hydrocarbon from an Aromatic Amine.—Parabromtoluene,



$$C_6H_4\begin{cases}CH_3 & (1)\\ Br & (4)\end{cases}.$$

Literature.—Hübner, Wallach: Ann., 154, 293; Glinzer, Fittig: *Ibid,* 136, 301; Michaelis, Genzken: *Ibid,* 242, 165; Ladenburg: Ber., 7, 1685; Sandmeyer: *Ibid,* 17, 2652; Schramm: *Ibid,* 18, 606; Gasiorowski u. Wayss: *Ibid,* 18, 1936; Gattermann: *Ibid,* 23, 1218; Erdmann: Ann., 272, 141; Heller: Z. angew. Chem., 23, 389.

25 grams copper sulphate.
72 grams potassium bromide.
9 grams (5 cc.) sulphuric acid (1.84).
10 grams reduced copper or copper bronze, "Natur Kupfer C."
160 grams water.

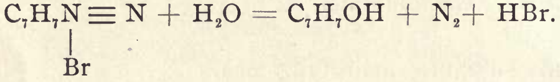
21.4 grams para-toluidine.
80 cc. water.
29 grams sulphuric acid (15.7 cc).
100 grams ice.

14 grams sodium nitrite.
70 cc. water.

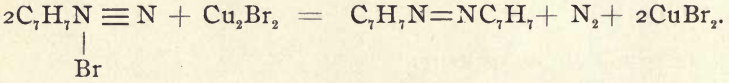
In a liter flask put 25 grams (1 mol.) of crystallized copper sulphate, 72 grams (6 mols.) of potassium bromide, 100 cc. of water, 10 grams of reduced copper, or copper bronze, "Natur Kupfer C," and 9 grams (5 cc., 1 mol.) of concentrated sulphuric acid. Heat on an asbestos plate with an upright condenser to gentle boiling till the solution is colorless. Meanwhile put in a beaker 21.4 grams (2 mols.) of paratoluidine, add 80 cc. of water and 29 grams (15.7 cc., 3 mols.) of concentrated sulphuric acid. The toluidine should dissolve in the hot solution to insure its complete conversion into the sulphate. Stir and cool till the sulphate has separated in finely divided condition. Add 100 grams of ice and, when the temperature has fallen to 0°, add slowly, with stirring, 14 grams (2 mols.) of sodium nitrite dissolved in 70 cc. of water. After standing for five minutes the solution should react for nitrous acid when a drop is placed on starch potassium iodide paper. If it does not, a little more of the nitrite must be added, but the least possible excess must be used. Neither the diazonium solution, nor that of the cuprous bromide should be allowed to stand long after they are prepared, because of the tendency of the former to decompose, and of the latter to oxidize.

Cool the cuprous bromide solution very slightly, and add the diazonium solution slowly, shaking vigorously and warming the solution on a vigorously boiling water-bath. The whole of the solution should be added within two to three minutes, if possible without cooling it too far. The diazonium solution is best added through a funnel with a long, wide stem dipping beneath the cuprous bromide solution.

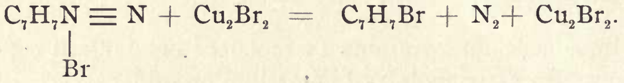
It is impossible in any case, apparently, to secure a perfectly clean reaction. Three different reactions may take place:



$$C_7H_7\underset{\overset{|}{Br}}{N}\equiv N + H_2O = C_7H_7OH + N_2 + HBr.$$



$$2C_7H_7\underset{\overset{|}{Br}}{N}\equiv N + Cu_2Br_2 = C_7H_7N{=}NC_7H_7 + N_2 + 2CuBr_2.$$



$$C_7H_7\underset{\overset{|}{Br}}{N}\equiv N + Cu_2Br_2 = C_7H_7Br + N_2 + Cu_2Br_2.$$

The first reaction takes place if the diazonium solution decomposes before it is added to the cuprous bromide, or if it is added to the hot solution in such a manner that it is not immediately mixed with it, so that the diazonium compound has no opportunity to combine with the cuprous bromide. Hence the necessity of vigorous shaking to secure a rapid and thorough mixture of the solutions. The second reaction is apparently favored when the diazonium-cuprous bromide remains in the cool solution undecomposed. The best conditions for the reaction appear to be secured at the lowest temperature of rapid decomposition for the diazonium-cuprous compound. This temperature varies in different cases. It is much higher for toluene para diazonium-cuprous bromide than for the ortho compound, apparently because of the greater stability of the former. (See Erdmann: *loc. cit.*)

When the diazonium solution has all been added, distil over the parabromtoluene in a rapid current of water vapor (see **22**, p. 71), shake it with some sodium hydroxide solution to remove any paracresol present, separate it from the solution, dry by allowing it to stand for some time with solid caustic potash, pour off or filter through a dry filter, and distil from a small distilling bulb, using a condensing tube or distilling slowly into a bottle or tube. Yield about 20 grams.

Parabromtoluene crystallizes in rhombic plates, which melt at 28.5°. It boils at 185.2°, and has a specific gavity of 1.3897 at $\frac{20^\circ}{4^\circ}$. Oxidizing agents convert it into parabrombenzoic acid.

93. **Preparation of a Bromine Derivative of an Acid. Hell-Volhard-Zelinsky's Method.**—α-Bromobutyric acid, $CH_3CH_2CHBr.CO_2H$. Bromo (2)-butanoic acid.

Literature.—Borodin: Ann., **119**, 121; Naumann: *Ibid*, **119**, 115; Hell: Ber., **14**, 891; **21**, 1726; Volhard: Ann., **242**, 141; Ber., **21**, 1904; Zelinsky: *Ibid*, **20**, 2026; Auwers and Bernhardi: *Ibid*, **24**, 2216; Hell and Lauber: *Ibid*, **7**, 560.

17.6 grams butyric acid.
2.2 grams red phosphorus.
60 grams bromine (20 cc.).

Select a small Liebig condenser whose inner tube will pass just inside of the neck of a 50 cc. round-bottomed flask. Cut off the lip of the flask, put the end of the condenser in its mouth and connect by means of a rubber tube, which slips over both, as is done with some forms of condensers. (See Fig. 39). Put in the flask 2.2 grams (⅓ at.) of red phosphorus, and 17.6 grams (1 mol.) of normal butyric acid. Add slowly from a dropping tube with a glass stop-cock, or from a bulb drawn out to a capillary below, through the top of the condenser, 60 grams

($^{11}/_3$ at.) of bromine. The bromine is best measured from a dry burette or measuring tube, in a good hood or out of doors. The top of the condenser should be closed with a doubly perforated stopper, one hole carrying the dropping tube, and the other a tube leading out of doors or just over the surface of a solution of caustic soda in a bottle. Drop in the bromine slowly, and warm very gently on a water-bath till the vapors of bromine disappear, usually about an hour. Cool, and pour the contents of the flask, in small portions, upon 50 grams of ice in a flask.

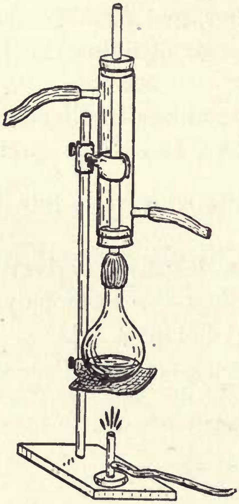
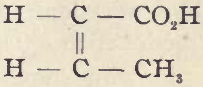


Fig. 39.

Shake vigorously, keeping the contents of the flask cold, till the bromide of the bromobutyric acid is decomposed, and the odor of phosphorus oxybromide has disappeared. Separate the acid from the aqueous solution, wash it once with a small amount of water, and distil it under diminished pressure. The portion boiling at 135°-140°, under a pressure of 35 mm. will be nearly pure.

In working with a small amount of acid the bromination may be effected with advantage by putting a weighed quantity of the acid in a sealed tube, converting it into the chloride by the calculated amount of phosphorus pentachloride, putting in a bulb containing two atoms of bromine for one molecule of the acid, sealing the tube, breaking the bulb containing the bromine by shaking the tube, and heating, till vapors of bromine disappear, in a water-bath. On cooling and opening the tube the phosphorus oxychloride may be decomposed by shaking with cold water and, in case the chloride of the acid is not readily decomposed in this way, it may be taken up with ether, the solution dried with calcium chloride, the ether distilled, and the chloride decomposed by warming with glacial formic acid. See Baeyer: Ann., **245**, 175; Aschan: *Ibid,* **271**, 265.

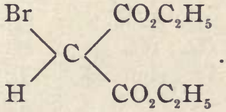
α-Bromobutyric acid boils with some decomposition at 212°-217°. It boils without decomposition at 136°-138° under a pressure of 35 mm. The specific gravity at 15° is 1.54. It dissolves in about 15 parts of water. When treated with alcoholic potash it is converted into cis-crotonic acid,



$$\begin{matrix} H - C - CO_2H \\ \| \\ H - C - CH_3 \end{matrix}$$

The yield is, however, poor, owing to the formation of hydroxybutyric acid and other substances.

94. **Preparation of the Bromine Derivative of an Ester by Direct Bromination.**—Ethyl ester of monobromomalonic acid.



Literature.—Knoevenagel: Ber., **21**, 1356; Conrad and Brückner: Ber., **24**, 2997; Condensation to ethylene tetracarboxylic ester (Dicarbintetracarboxyl ester) Blank and Sampson: Ber., **32**, 860.

30 grams ethyl malonic ester.

30 grams (9.6 cc.) bromine.

Put in a 100 cc. distilling bulb 30 grams of malonic ester. Insert in the neck of the bulb a rubber stopper bearing a separatory funnel. Put in the separatory funnel 30 grams (1 mol. = 9.6 cc.) of bromine. Connect the side tube of the bulb with a tube which will deliver the hydrobromic acid evolved over water in a 500 cc. bottle but the tube *should not dip below the surface* *of the water.* The whole operation should be carried out in a good hood. Drop the bromine into the ester slowly with constant shaking and warming at first to 40°-50° to start the reaction. After all of the bromine has been added warm gently for a short time, on the water-bath, till the mixture becomes nearly colorless. Cool thoroughly, add in small portions with constant cooling a ten per cent. solution of sodium carbonate till the solution remains alkaline to litmus after shaking. Transfer to a separatory funnel and draw off the bromomalonic ester below, first filling the funnel nearly full of water and agitating gently so that none of the heavy liquid floats in globules on the surface. Dry the ester with calcium chloride, pour off or filter into a Claissen distilling bulb (p. 172) and distil under diminished pressure. The portion boiling at 120°-125° under a pressure of 14 mm. is sufficiently pure for most purposes but retains some dibromomalonic ester which cannot be entirely removed by fractionation. The diethylester of bromomalonic acid boils at 235° with some decomposition and has a specific gravity of 1.426 at 15°.

95. **Preparation of a Chlorine Derivative of a Hydrocarbon by the Use of Calcium Hypochlorite.**—Chloroform, $CHCl_3$, trichloromethane.

Literature.—Soubeiran: Ann. chim. phys. [2], **48**, 131 (1831); Liebig: Ann., **1**, 199; Belohoubek: *Ibid,* **165**, 349; Goldberg: J. prakt. Chem. [2], **24**, 109 (1881); Bechamp: Ann. chim. phys. [5], **22**, 347 (1881); Orndorff and Jessel: Am. Chem. J., **10**, 365; E. R. Squibb: J. Am. Chem. Soc., **18**, 231.

150 grams bleaching powder.
450 cc. water.

12 grams (16 cc.) acetone.
35 cc. water.

Put in a liter flask 150 grams of bleaching powder (containing 33 per cent. available chlorine), add 450 cc. of water, and insert a stopper bearing a dropping funnel, a bent tube leading to a condenser, and a third tube leading nearly to the bottom of the flask. Introduce through the dropping funnel, slowly and with frequent shaking, a mixture of 16 cc. of acetone with 35 cc. of water. After the acetone has all been added and the flask no longer grows warm spontaneously, distil the remainder of the chloroform by passing in a current of steam. Shake the chloroform several times with small quantities of water, separate, dry by allowing to stand with fused calcium chloride, and distil from the water-bath without separating from the calcium chloride. Yield about 20 grams.

Chloroform is a colorless liquid with an ethereal odor and a sweetish taste. It boils at 61°, and has a specific gravity of 1.5039 at $\frac{11.8^\circ}{4^\circ}$, and of 1.5264 at $\frac{0^\circ}{4^\circ}$. Pure chloroform decomposes slowly, especially in the sunlight, with liberation of chlorine, hydrochloric acid, phosgene, and other substances. The addition of one per cent. of alcohol renders it more stable. Pure chloroform should not impart an acid reaction to water with which it is shaken, nor should it react with a solution of silver nitrate in the cold.

96. Preparation of an Iodine Derivative of a Hydrocarbon by the Action of Iodine and Sodium Carbonate on Ethyl Alcohol.

—Iodoform, CHI_3, triiodomethane.

Literature.—Serullas: Ann. chim. phys. [2], **22**, 172; **25**, 311; Bouchardat: Ann., **22**, 225; Spindler: Ann., **231**, 263; Förster, Meyer: J. prakt. Chem. [2], **56**, 354; Elbs, Herz: Chem. Zentralbl, **1897**, II, 695: Quantitative determination, Greshoff: Z. anal. Chem., **29**, 209; **32**, 361; Schacherl: Chem.-Zentralbl, 1897, I, 568.

10 grams crystallized sodium carbonate (or 3.6 grams of the anhydrous salt).
50 cc. water.
10 grams alcohol.
10 grams iodine.

In a 100 cc. flask dissolve 10 grams of crystallized sodium carbonate (or 3.6 grams of the anhydrous salt) in 50 cc. of warm water, add 10 grams of alcohol, warm to 70°-80° and add in portions 10 grams of iodine, but do not add iodine after the iodine color no longer disappears after warming for a short time.

Cool, filter and wash the iodoform. Dissolve it in 15-20 cc. of ether, wash the solution twice with water, dry it with calcium chloride and allow the ether to evaporate spontaneously in a small beaker or crystallizing dish. Yield 2-3 grams.

Iodoform crystallizes in leaflets or in hexagonal plates which melt at 119°. It is volatile with water vapor and is a powerful germicide.

Chapter XII

NITRO COMPOUNDS

The nitro derivatives of aromatic compounds have been longest known and are most easily prepared. For a long time it was thought that nitro derivatives of hydrocarbons of the marsh gas series could not be prepared by the direct treatment of hydrocarbons with nitric acid. Konowalow has shown, however, (Ber., 28, 1852, and 29, 2199), that such compounds may, in many cases, be prepared by the use of dilute nitric acid, and nitro compounds of the homologues of benzene may be prepared containing the nitro group in the side chain by the same method.

The method more usually employed for the preparation of nitro compounds of the aliphatic series consists in treating alkyl iodides with silver nitrite.

$$RI + AgNO_2 = R—NO_2 + AgI.$$

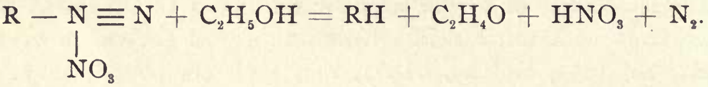
With aromatic hydrocarbons nitration is effected sometimes by adding the hydrocarbon or other compound to the nitric acid, and sometimes by the reverse process.

$$RH + HNO_3 = RNO_2 + H_2O.$$

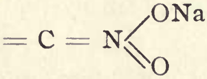
As the reaction is accompanied by a considerable evolution of heat, the mixture must usually be made carefully, and in many cases cooling is necessary. The strength of acid and the temperature required vary greatly in different cases. Sometimes it is necessary to reinforce the acid by the use of a mixture with concentrated sulphuric acid. In general it is better to use such a mixture and moderate the action by cooling rather than to use nitric acid alone at a higher temperature. Benzene derivatives with side chains are more easily nitrated than benzene itself.

The nitro group usually enters in the para or ortho position with reference to CH_3, C_2H_5, OH, NH_2, Cl, Br, or I, but mainly in the meta position toward CO_2H, SO_3H, CHO, CN, CCl_3, or NO_2. In the case of the amino group it is sometimes possible to cause the group to enter in the ortho or meta position at will by changing the conditions, or by introducing the acetyl group in the amino group.

In order to secure a nitro group in a desired position it is often necessary to introduce two groups, and then eliminate one of them by reduction to the amino group and subsequent elimination of the latter through the diazonium reaction.



$$R - \underset{\substack{| \\ NO_3}}{N} \equiv N + C_2H_5OH = RH + C_2H_4O + HNO_3 + N_2.$$

Primary and secondary nitro compounds are soluble in solutions of alkalies with the formation of salts having the structure,  (Nef: Ann., **280**, 263; Ber., **29**, 1218). Tertiary nitro compounds, and nitro compounds of the aromatic series except nitrophenols (Hantsch), do not form compounds of this character.

Mononitro compounds of benzene and its homologues are volatile with water vapor, and may frequently be separated from dinitro compounds and other substances by this means.

The reduction of nitro compounds to amines and other compounds will be considered in the following chapter.

The nitration of toluene has already been given on p. 126.

97. Nitration of an Aromatic Hydrocarbon.—Nitrobenzene.

Literature.—Mitscherlich: Ann., **12**, 305.

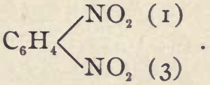
50 grams of benzene.
60 grams nitric acid (1.42).
80 grams sulphuric acid (1.84).

Put 50 grams of benzene in a 300 cc. flask. Drop in slowly, with vigorous shaking and during about 15 minutes a *cooled* mixture of 60 grams of nitric acid (1.42) and 80 grams of sulphuric acid (1.84). Cool in running water so that the temperature does not rise above 50°-60°. When all of the acid has been added and the temperature no longer rises on vigorous shaking, place the flask on the water-bath and heat for half an hour with frequent shaking. Cool again, pour the contents of the flask into 300 cc. of cold water, separate the nitrobenzene from the acid solution, wash it once with water, dry with calcium chloride and distil.

Nitrobenzene solidifies at a low temperature and melts at 5°. It boils at 210° and has a specific gravity at ${}^{20^\circ}/_{4^\circ}$ of 1.2033.

98. Preparation of a Dinitro Compound by Direct Nitration.—

m-Dinitrobenzene,



$C_6H_4\begin{cases}NO_2 & (1)\\ NO_2 & (3)\end{cases}$.

Literature.—Deville: Ann. chim. phys., [3], 3, 187 (1841); Muspratt, Hofmann: Ann., 57, 214; Beilstein, Kurbatow: *Ibid*, 176, 43; Willgerodt: Ber., 25, 608; V. Meyer, Stadler: *Ibid*, 17, 2649.

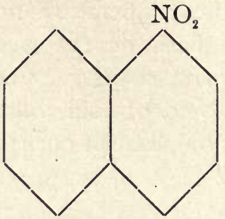
20 grams benzene (23 cc.).
50 cc nitric acid (1.42).
50 cc. concentrated sulphuric acid.

100 cc. concentrated sulphuric acid.

Put in a 300 cc. flask 20 grams (23 cc.) of benzene and add in small portions a cooled mixture of 50 cc. of nitric acid (sp. gr. 1.42) with 50 cc. of concentrated sulphuric acid. Shake vigorously after each addition and cool somewhat, to prevent too violent a reaction. When the mixture has all been added and the whole shaken vigorously for some minutes, add in small portions and shaking as before, but without cooling, 100 cc. of concentrated sulphuric acid. Heat to about 120°, allow to cool to about 80°, and pour, with stirring, into 1500 cc. cold water. Filter off the dinitrobenzene and crystallize from alcohol. Yield 30 to 32 grams.

Metadinitrobenzene crystallizes in needles which are colorless and odorless. It melts at 91° and boils without decomposition at 297°. 100 parts of alcohol at 20° dissolve 3.5 parts. Easily soluble in hot alcohol. Practically insoluble in water.

99. α-Nitronaphthalene,



Literature.—Laurent: Ann. chim. phys., [2], 59, 378; Beilstein, Kuhlberg: Ann., 169, 83; Liebermann: *Ibid,* 183, 235; Piria: *Ibid,* 78, 32; Aguiar: Ber., 5, 370.

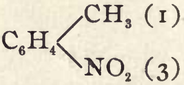
20 grams naphthalene.
100 grams nitric acid (sp. gr. 1.33).
or
55 cc. nitric acid (sp. gr. 1.42).
25 cc. water.

Put in a beaker 20 grams of naphthalene, add 100 grams (75 cc.) of nitric acid (sp. gr. 1.33) and allow to stand for several days. Dilute with water, filter, wash and dry. Moisten with a very little alcohol and treat with carbon bisulphide, which dissolves the mononitro compound. Filter from the insoluble dinitro compound, and evaporate the solution to dryness. (*Beware of flames.*) The solution can be evaporated on a previously heated water-bath in a hood, all flames in the neighborhood being extinguished. Recrystallize from alcohol. Yield 17 grams.

α-Nitronaphthalene crystallizes in fine yellow needles which melt at 61°. It boils at 304°. It gives by oxidation nitrophthalic acid, while the aminonaphthalene obtained by its reduction gives by oxidation phthalic acid.

By reduction it gives α-naphthtylamine which is used for the determination of nitrites in potable waters.

100. Preparation of a Nitro Derivative of an Amine and Elimination of the Amino Group.—*m*-Nitrotoluene,



$C_6H_4 < \begin{matrix} CH_3\ (1) \\ NO_2\ (3) \end{matrix}$.

Literature.—Monnet, Reverdin, Nölting: Ber., 12, 443; Nölting, Witt: *Ibid,* 18, 1336; Buchka: *Ibid,* 22, 829; Noyes, Moses: Am. Chem. J., 7, 149; Noyes: *Ibid,* 10, 475; Schraube, Romig: Ber., 26, 579.

20 grams paraacetotoluide.
75 cc. nitric acid (1.42).
30 cc. concentrated sulphuric acid.

50 cc. alcohol.
10 grams potassium hydroxide.
13 cc. water.

15 grams nitrotoluidine.
60 cc. absolute alcohol.
12 cc. concentrated sulphuric acid.
8 grams (9 cc.) ethyl nitrite.

Prepare acetotoluide by boiling paratoluidine with twice its weight of glacial acetic acid for two hours (see acetanilide, p. 157), pouring into cold water, filtering off, washing and drying. Add 20 grams of the finely powdered substance in small portions to a mixture of 75 cc. of nitric acid with 30 cc. of concentrated sulphuric acid. Stir with a thermometer during the addition, and keep the temperature between 30° and 40° by setting the beaker in cold water. When all has been added allow the beaker to stand for fifteen minutes and then pour the mixture into cold water, filter off the nitroacetotoluide, wash and suck and press as dry as possible on a plate. Put the substance in a flask, add 50 cc. of alcohol, heat nearly to boiling, and add carefully a solution of 10 grams of potassium hydroxide in 13 cc. of water. Heat on a water-bath for twenty minutes. Cool thoroughly, filter off the nitrotoluidine on a plate, wash with alcohol diluted with two volumes of water, and dry thoroughly.

Put 15 grams of the nitrotoluidine in a 300 cc. flask and add a warm mixture of 60 cc. of absolute alcohol with 12 cc .of concentrated sulphuric acid; cool thoroughly and add slowly with vigorous shaking and cooling, 7.5 grams of ethyl nitrite (see **122**, p. 250). Allow to stand a few minutes, and then warm on the water-bath till the evolution of nitrogen ceases. Cool, precipitate the nitrotoluene by adding water, siphon off or decant most of the aqueous solution, and distil the nitrotoluene which remains, in a current of steam (see **22**, p. 71). A small amount of nitrotoluene may be obtained by extracting the alcoholic mother-liquors with ether, but in most cases it is not worth while to do that. Separate the nitrotoluene from the water of the distillate, and dry it *in vacuo* over sulphuric acid. Yield 8 to 10 grams.

Instead of the method given here, Meyer and Jacobson advise in their text-book (Vol. II, p. 158) to dissolve the nitrotoluidine in a mixture of three parts of alcohol and three parts, by weight, of concentrated sulphuric acid, cool, add the theoretical amount of sodium nitrite dissolved in the smallest possible amount of water, and then warm on the water-bath as above. In our experience the yields obtained in this way are much less.

Instead of adding ethyl nitrite, the mixture of nitric oxide and nitrogen peroxide (usually called nitrous anhydride), obtained by boiling arsenious oxide with nitric acid (sp. gr. 1.30-1.35), may be passed into the acid alcoholic solution till it smells strongly of the nitrous ester after standing a short time, or ethyl nitrite may be passed in as it is generated at such a temperature as to assume the gaseous form (see **122**, p. 250).

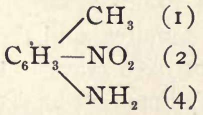
Paraacetotoluide crystallizes in rhombic needles which melt at 153°. It boils at 307°.

3-Nitro-4-acetotoluide crystallizes from water in fine yellow needles which melt at 94°-95°.

3-Nitro-4-toluidine crystallizes in red prisms, which melt at 116°-117°. It is volatile with water vapor.

Meta-nitrotoluene melts at 16°, and boils at 230°-231°. By the chromic acid mixture it is oxidized to meta-nitrobenzoic acid. By an alkaline solution of potassium ferricyanide it is much less easily oxidized than ortho- or paranitrotoluene.

101. Preparation of a Nitro Derivative of an Amine.—*p*-amino-*o*-nitrotoluene,



$$C_6H_3\begin{cases} CH_3 & (1) \\ NO_2 & (2) \\ NH_2 & (4) \end{cases}.$$

Literature.—Beilstein, Kuhlberg: Ann., 155, 23; Nölting and Collin: Ber., 17, 263; Noyes, Moses: Am. Chem. J., 7, 150.

10 grams *p*-toluidine.
100 grams concentrated sulphuric acid (sp. gr. 1.84).
7.5 grams nitric acid (sp. gr. 1.48).
30 grams concentrated sulphuric acid.

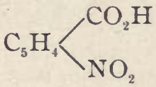
500 cc. ice-water.
400 grams acid sodium carbonate.

Dissolve 10 grams of paratoluidine in 200 grams (120 cc.) of cold concentrated sulphuric acid. Cool to 0° with a freezing mixture (the most convenient is snow or ice and concentrated commercial sulphuric acid, snow and salt is a little cheaper), and drop in slowly a mixture of 7.5 grams (5 cc.) of nitric acid (sp. gr. 1.48), with 30 grams (17 cc.) of concentrated sulphuric acid, stirring and keeping the temperature below 5°. Allow the mixture to stand for half an hour, and pour into 500 cc. of ice-water, keeping the temperature below 25°. Filter, add 1000 cc. of water and neutralize with baking soda. About 400 grams will be required. Filter off and wash the precipitated nitrotoluidine, and crystallize from dilute alcohol. Yield about 10 grams.

In this nitration the large amount of sulphuric acid forms an acid sulphate with the toluidine, and appears in that way to so change the character of the amino group that the nitro group enters in the meta position with regard to it. Compare the preceding preparation.

Orthonitroparatoluidine crystallizes from water in broad, yellow, monoclinic needles, which melt at 77.5°.

102. Preparation of a Nitro Derivative of an Aromatic Acid.—

Meta-nitro-benzoic acid,


$$C_5H_4\left\langle\begin{array}{ll} CO_2H & (1). \\ NO_2 & (3). \end{array}\right.$$

Literature.—Mulder: Ann., 34, 297; Gerland: *Ibid*, 91, 186; Griess: Ber., 8, 526; 10, 1871; Widmann: Ann. 193, 202; C. Liebermann: Ber., 10, 862; Ernst: Ztschr. chem., *1860*, 477.

25 grams benzoic acid.
50 grams potassium nitrate.
75 grams absolute sulphuric acid (monohydrate).

Warm 75 grams of absolute sulphuric acid[1] to 70° in a beaker, and add, in small portions, a powdered mixture of 25 grams of benzoic acid and 50 grams of potassium nitrate, stirring vigorously and keeping the temperature at 80°-90°. When all has been added, and the nitrobenzoic acid has separated as an oily layer on the surface of the liquid, pour the contents of the beaker into a porcelain dish, and allow the product to solidify. Separate the cake of nitro acids from the acid potassium sulphate. Put the nitro acids (about 75 per cent. of meta, 22 per cent. of the ortho, and 2½ per cent. of the para acids are present in the mixture) in a beaker with 100 cc. of water, heat till the acids melt, and stir thoroughly. Cool, filter, and wash with cold water. Dissolve the acid, in 300-400 cc. of hot water, and add a clear concentrated solution of barium hydroxide (about 30 grams) to alkaline reaction. Cool, filter, and wash. The barium salts of the ortho and para acids pass into the filtrate, while a part of the ortho acid remained in solution on treatment with water before. The pure meta acid can be obtained by treating the barium salt with 200 cc. of hot water and some sulphuric acid, filtering hot from the barium sulphate, which separates, and cooling the filtrate.

Meta-nitro-benzoic acid melts at 141°-142°. It dissolves in 10 parts of hot water, and in 425 parts of water at 16.5°. It is very easily soluble in alcohol and ether. The barium salt is soluble in 19 parts of boiling water, and in 265 parts of cold water.

The ortho and para acids may also be separated from the mixture obtained by the nitration of benzoic acid, but are more readily obtained by the oxidation of the nitro-toluenes. (See 51, p. 126.)

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[1] Absolute sulphuric acid, called technically the "monohydrate," can be purchased or may be prepared by cooling concentrated sulphuric acid to 0° or below, until it crystallizes and pouring off the liquid portion, the crystals consisting of absolute sulphuric acid, if the acid is sufficiently strong. The crystallization may be started with crystals obtained by cooling a mixture of ordinary sulphuric acid with the fuming acid.

Chapter XIII

AMINES

The simplest method of preparing amines, and one which usually gives pure compounds, consists in reducing nitro compounds.

$$RNO_2 + 6H = RNH_2 + 2H_2O.$$

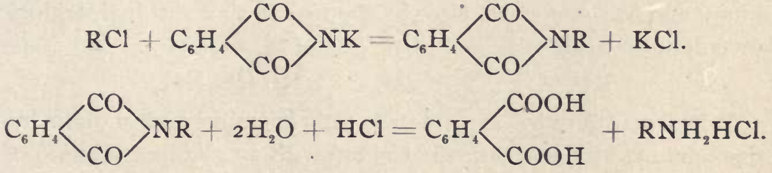
The reducing agents generally used are tin and hydrochloric acid, iron and acetic acid (in manufacture), ammonium sulphide, and stannous chloride. This method of preparation is general with aromatic compounds, but is not often used for members of the marsh gas series, because of the difficulty of obtaining the nitro compounds required.

A method of great historical importance consists in treating halogen derivatives with an aqueous solution of ammonia.

$$RBr + NH_3 = RNH_2HBr.$$

The ease with which secondary and tertiary amines, and quaternary ammonium salts are formed by this reaction detracts from its usefulness, as the resulting mixtures are often difficult of separation. (For a method of separation see pp. 160 and 267.)

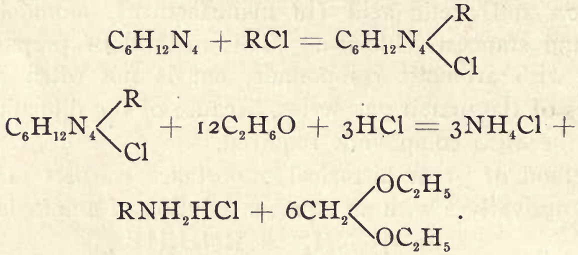
To overcome the difficulty which arises from the formation of secondary and tertiary amines when halogen compounds are treated with ammonia, Gabriel has used, successfully, potassium phthalimide. When this is heated with halogen compounds to 150°-200° in sealed tubes or open vessels, according to the nature of the halogen compound, derivatives of the phthalimide are formed. These may be saponified with separation of the chloride of the primary amine by heating in sealed tubes at 200°, with three parts of fuming hydrochloric acid. (Ber., **20**, 2224; **21**, 566, 2669.),



$$RCl + C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NK = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NR + KCl.$$

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NR + 2H_2O + HCl = C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right. + RNH_2HCl.$$

Another method of attaining the same end, which seems very general in its application, has been worked out by Delepine (Compt. rend., **120**, 501; **124**, 292). On heating hexamethylene amine with halogen compounds in solution in chloroform, double compounds are produced. When these are heated gently with alcohol and concentrated hydrochloric acid they are decomposed with the formation of a primary amine and methylene-diethyl ether.

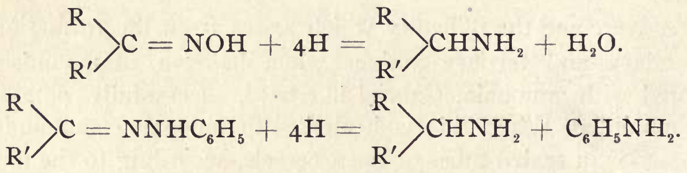


$$C_6H_{12}N_4 + RCl = C_6H_{12}N_4\!\left\langle\begin{array}{l}R\\Cl\end{array}\right.$$

$$C_6H_{12}N_4\!\left\langle\begin{array}{l}R\\Cl\end{array}\right. + 12C_2H_6O + 3HCl = 3NH_4Cl + RNH_2HCl + 6CH_2\!\left\langle\begin{array}{l}OC_2H_5\\OC_2H_5\end{array}\right. .$$

The method has been successfully used for the preparation of benzyl amine and of allyl amine.

A very useful method consists in the reduction of oximes and hydrazones.



$$\left.\begin{array}{r}R\\R'\end{array}\right\rangle C = NOH + 4H = \left.\begin{array}{r}R\\R'\end{array}\right\rangle CHNH_2 + H_2O.$$

$$\left.\begin{array}{r}R\\R'\end{array}\right\rangle C = NNHC_6H_5 + 4H = \left.\begin{array}{r}R\\R'\end{array}\right\rangle CHNH_2 + C_6H_5NH_2.$$

The best reducing agent for the oximes appears to be absolute alcohol and sodium. The same method may also be applied to hydrazones, or the latter may be reduced by zinc dust and acetic acid in alcoholic solutions.

Nitriles may be reduced to amines by absolute alcohol and sodium, and in some cases, also, by the use of zinc and hydrochloric or sulphuric acid.

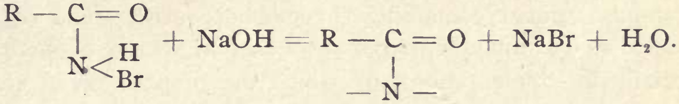
$$R - C \equiv N + 4H = R{-}CH_2NH_2.$$

When acid amides are treated with bromine and sodium hydroxide, or, in many cases, if treated with an alkaline solution of sodium hypobromite, they are converted into amines with loss of carbon dioxide.

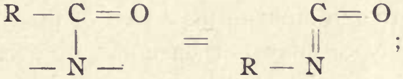
$$R{-}CONH_2 + NaOBr + 2NaOH = RNH_2 + NaBr + H_2O + Na_2CO_3.$$

The most plausible explanation of this reaction appears to be that given by Stieglitz, based on the work of Nef (Am. Chem. J., 18, 751).

$$R{-}CONH_2 + NaOBr \ = \ R{-}CO{-}NHBr + NaOH.$$



$$\begin{array}{l} R-C=O \\ \quad\ | \\ \quad\ N{<}^{H}_{Br} \end{array} + NaOH = \begin{array}{c} R-C=O \\ \qquad | \\ \qquad -N- \end{array} + NaBr + H_2O.$$



$$\begin{array}{c} R-C=O \\ \quad | \\ \ -N- \end{array} = \begin{array}{c} C=O \\ \| \\ R-N \end{array};$$

$$RN = CO + H_2O = RNH_2 + CO_2.$$

Lengfeldt, Stieglitz, and Elizabeth Jeffreys have shown (Ber., 30, 898; see also Am. Chem. J., 15, 215, 504; 16, 307; 19, 295) that in the case of aliphatic amides of high molecular weights, where the reaction cannot be applied in its usual form owing to the formation of nitriles, the urethane can be obtained by dissolving the amide (1 molecule) in 3 parts of methyl alcohol, adding a solution of sodium (2 atoms) in 25 parts of methyl alcohol, and dropping bromine (2 atoms) into the solution. After warming for ten minutes on the water-bath, the solution is acidified with acetic acid, evaporated, the inorganic salts removed with water and the urethane separated from unchanged amide by solution in warm ligroin. The urethane is decomposed by heating with concentrated sulphuric acid at 110°-120° for an hour, or, better, by distilling with three to four times its weight of slaked lime.

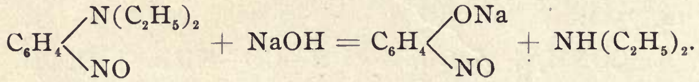
$$RCONHBr + NaOCH_3 = \underset{\text{Urethane}}{RNHCOOCH_3} + NaBr.$$

$$RNHCOOCH_3 + Ca(OH)_2 = RNH_2 + CaCO_3 + CH_3OH.$$

Aromatic amines may sometimes be prepared from phenols by heating with concentrated ammonia in sealed tubes or by heating with ammonia and zinc or calcium chloride.

$$ROH + NH_3 = RNH_2 + H_2O.$$

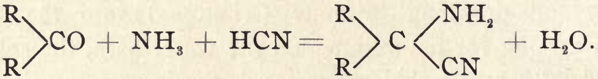
Dimethyl and diethyl amine can be prepared with advantage by decomposing *p*-nitrosodimethyl- or diethylaniline with caustic soda.



$$C_6H_4\left\langle\begin{array}{l}N(C_2H_5)_2\\ NO\end{array}\right. + NaOH = C_6H_4\left\langle\begin{array}{l}ONa\\ NO\end{array}\right. + NH(C_2H_5)_2.$$

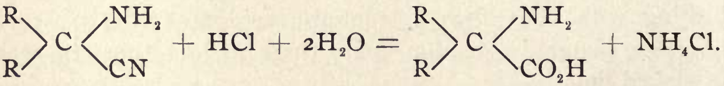
Complex amines containing chromophore groups and of importance as dyes may be prepared by a great variety of methods, especially by condensations, of which the preparation of malachite green (p. 241) is an illustration. Heterocyclic compounds in which the nitrogen atom forms a part of the ring and in which the nitrogen may or may not have the property of combining with acids to form salts are also prepared in many ways. The preparation of pyridine, piperidine, quinoline, p. 238), indigo, (p. 235), and collidine dicarboxylic acid ester are typical of many similar preparations.

When a ketone or aldehyde is treated with a concentrated aqueous solution of potassium cyanide and ammonium chloride the hydrocyanic acid and ammonia, present in such a solution by hydrolysis, condense with the ketone or aldehyde to form an α-amino nitrile. (Zelinsky, Stadnikoff. Ber., 39, 1726).



$$\begin{array}{l}R\\ R\end{array}\Big\rangle CO + NH_3 + HCN = \begin{array}{l}R\\ R\end{array}\Big\rangle C\left\langle\begin{array}{l}NH_2\\ CN\end{array}\right. + H_2O.$$

The nitrile may be saponified to an α-amino acid by hydrochloric acid.



$$\begin{array}{l}R\\ R\end{array}\Big\rangle C\left\langle\begin{array}{l}NH_2\\ CN\end{array}\right. + HCl + 2H_2O = \begin{array}{l}R\\ R\end{array}\Big\rangle C\left\langle\begin{array}{l}NH_2\\ CO_2H\end{array}\right. + NH_4Cl.$$

103. **The Preparation of an Amine by the Reduction of a Nitro Compound.**—Aniline, $C_6H_5NH_2$.

Literature.—Unverdorben: Pogg. Ann., 8, 397; Runge: Pogg. Ann., 31, 65; 32, 331; Fritsche: Ann., 36, 84; 39, 76; Anderson: *Ibid*, 70, 32; Hofmann: *Ibid*, 55, 200; 53, 11; Wöhler: *Ibid*, 102, 127; Merz, Weith:

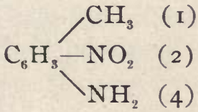
Ber., 13, 1298; Merz, Müller: *Ibid,* 19, 2916; Reverdin, Harpe: *Ibid,* 22, 1004.

25 grams nitrobenzene.
45 grams tin.
100 cc. commercial hydrochloric acid.

Put into a 500 cc. flask 25 grams of nitrobenzene and 45 grams of tin. Add about 10 cc. of commercial hydrochloric acid, (sp. gr. 1.16), and shake vigorously. If the solution becomes so hot as to boil, cool it somewhat by dipping the flask in cold water. When the reaction moderates add 10 cc. more of the acid, and continue in the same manner till 100 cc. have been added Warm on the water-bath till the odor of nitrobenzene disappears. Cool, add, with further cooling if necessary, a solution of 75 grams of caustic soda in 100 cc. of water, and distil off the separated aniline with water vapor, distilling about 100 cc. after the distillate ceases to appear turbid. Add to the distillate 20 to 30 grams of salt and some ether, separate the ethereal solution, dry it by allowing it to stand for some time, best over night, with some powdered caustic potash, pour off into a distilling bulb, distil the ether from the water-bath, and then the aniline with a free flame. Yield 15 to 17 grams.

Aniline is a colorless oil with a slightly aromatic odor. It melts at —8°, boils at 183.7°, and has a specific gravity of 1.036 at 0°, and 1.0276 at 11.6°. Aniline forms salts which crystallize well, but these react acid toward test papers. Aniline dissolves in 31 parts of water at 12.5°. The hydrochloride is easily soluble in alcohol and in water, and melts at 192°. It is less easily soluble in hydrochloric acid, a characteristic which may be used with advantage in the crystallization and purification of many of the chlorides of organic bases. Aqueous solutions of aniline give a violet color on the addition of a few drops of a solution of calcium hypochlorite (chloride of lime).

104. Preparation of a Nitro-Amino Compound by the Reduction of a Dinitro Compound.—*p*-amino-*o*-nitrotoluene,



$$C_6H_3\begin{array}{l} /CH_3\ \ (1)\\ —NO_2\ \ (2)\\ \backslash NH_2\ \ (4)\end{array}.$$

Literature.—See 101, p. 214; also Beilstein and Kuhlberg: Ann., 155, 13

15 grams toluene.
35 cc. nitric acid (1.42).
35 cc. sulphuric acid.

75 cc. sulphuric acid.

15 grams dinitrotoluene.
50 cc. alcohol.
8 cc. ammonia. (0.90).
Hydrogen sulphide.

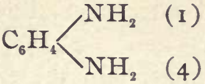
Put 15 grams of toluene in a small flask and add in small portions, 70 cc. of a mixture of equal volumes of concentrated sulphuric and concentrated nitric acids, shaking vigorously and cooling somewhat. After the mixture has all been added and the reaction moderates, add 75 cc. of concentrated sulphuric acid, shake vigorously, heat to about 130° and keep the mixture at that temperature, shaking vigorously for about 15 minutes. Allow to cool, pour into water, filter, wash, and crystallize the dinitrotoluene from alcohol. 20 to 25 grams of pure dinitrotoluene, melting at 70.5°, should be obtained.

Put 15 grams of the dinitrotoluene in a flask, add 50 cc of alcohol and 8 cc. of concentrated ammonia (0.90), pass in a rapid current of hydrogen sulphide nearly to saturation, connect the flask with a reversed condenser or condensing tube, and heat on a water-bath for half an hour. Cool, saturate again with hydrogen sulphide, and heat as before. Filter hot, cool the filtrate, add water, and filter off the precipitated nitrotoluidine after standing for some time. Purify by dissolving in dilute hydrochoric acid, filtering, and precipitating again with ammonia. Yield about 10 grams.

Orthonitroparatoluidine crystallizes from water in broad yellow monoclinic needles, which melt at 77.5°. It is difficultly soluble in water and carbon bisulphide, easily soluble in alcohol and acids.

105. Preparation of a Diamino Derivative of Benzene.—

p-Phenylenediamine,



$C_6H_4\begin{cases}NH_2 & (1)\\ NH_2 & (4)\end{cases}$

(*p*-Diaminobenzene).

Literature.—Grethen: Ber., **9**, 775; Beilstein, Kurbatow: Ann., **197**, 83; Nölting, Collins: Ber., **17**, 262; Hobrecker: *Ibid*, **5**, 920.

20 grams acetanilide.
75 cc. nitric acid (1.42).
30 cc. sulphuric acid (1.84).

20 grams nitroacetanilide.
30 grams tin.
80 cc. commercial hydrochloric acid.

Hydrogen sulphide.
Lime.

Prepare *p*-nitroacetanilide exactly as directed for nitroacettoluide (see p. 213). Put in a flask 20 grams of nitroacetanilide and 30 grams of tin. Add 10 cc. of concentrated commercial hydrochloric acid, and shake till the reaction begins to moderate; add more of the acid and shake as before, and continue till 80 cc. of acid have been added. Then heat on the water-bath till the reaction is complete. The nitro group is reduced and the acetyl group is also removed. Dilute with three or four volumes of water, pour off from any undissolved tin, precipitate the tin from the solution with hydrogen sulphide, and filter on a Witt Plate or Hirsch funnel (see p. 120). The hydrogen sulphide is best generated in a two-liter acid bottle from considerably more than the theoretical amount of iron sulphide, which is placed in the bottle with 1500 cc. of water. Somewhat more than the theoretical amount of concentrated commercial sulphuric acid is then added, in small portions, through the thistle tube. The gas should be passed through a washing tube or wash-bottle containing a little water. After the operation is over, the generator should be emptied at once, as the ferrous sulphate would crystallize on standing. If any unused ferrous sulphide is left in the bottle, and the latter is filled up at once with water to prevent its oxidation, it can be saved for use again.

Evaporate the filtrate to a small volume, filter again, if necessary, through a hardened filter, and allow the chloride of the phenylenediamine to crystallize.

To prepare the free amine, mix the chloride with an equal weight of quicklime, and distil from a small retort. The paraphenylenediamine may be recrystallized from benzene. Yield 10 to 12 grams.

Paradiaminobenzene crystallizes from benzene in shining leaflets, which melt at 140° and boil at 260°. It is moderately soluble in hot water.

Paranitroacetanilide melts at 207°.

106. Preparation of an Amine by the Decomposition of an Alkyl Derivative of Aniline.—Diethylamine, $(C_2H_5)_2NH$.

Literature.—Hofmann: Ann., 74, 128, 135; Elsbach: Ber., 15, 690; Piutti: Ann., 227, 182; Pictet: Ber., 20, 3422; Schloemann: *Ibid,* 26, 1020; Reynolds: J. Chem. Soc., 61, 457; Kopp: Ber., 8, 621; Lippmann u. Fleissner: *Ibid,* 16, 1422; Hofmann: Ann., 73, 91; Wallach: *Ibid,* 214, 275; Reinhardt and Staedel: Ber., 16, 29; Baeyer and Caro: *Ibid,* 7, 963.

30 grams aniline.
45 grams ethyl bromide.

20 grams sodium hydroxide.
60 cc. water.

35 grams ethyl aniline.
45 grams ethyl bromide.

20 grams sodium hydroxide.
60 cc. water.

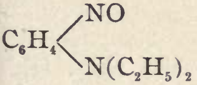
30 grams diethylaniline.
150 cc. water.
120 cc. concentrated hydrochloric acid (1.19).
100 grams ice.

16 grams sodium nitrite.
80 cc. water.

70 grams sodium hydroxide.
210 cc. water.

Put in a small flask 30 grams of aniline and 45 grams of ethyl bromide, and heat with a reversed condenser for one or two hours, or until the mass solidifies. Cool, add 60 cc. of a solution of sodium hydroxide (3 cc. = 1 gram), with cooling, separate the ethyl aniline, add to it 45 grams of ethyl bromide, and heat with reversed condenser as before, till the mass solidifies. Dissolve in water, boil to expel any ethyl bromide which remains, cool, add 60 cc. of caustic soda, and separate the diethyl aniline. Dry with powdered potassium hydroxide, and distil, collecting as much as possible of the portion boiling at 212°-215°. (Aniline boils at 183.7°, ethyl aniline at 206°, and diethyl aniline at 213.5°.)

Dissolve 30 grams of the diethyl aniline in 120 cc. of concentrated hydrochloric acid and 150 cc. of water, cool, add 100 grams of ice, and when the solution is near 0° add slowly, with stirring, 16 grams of sodium nitrite dissolved in 80 cc. of water. After an hour transfer the solution of nitrosodiethyl aniline,

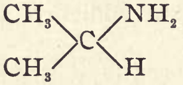


$C_6H_4\begin{cases} NO \\ N(C_2H_5)_2 \end{cases}$, to a liter flask and add carefully, with shaking, 210 cc. of a strong solution of sodium hydroxide, connect with a condenser by means of a bent tube, and distil, collecting the distillate in a flask containing 20 cc. of concentrated hydrochloric acid. The solution remaining in the flask may be used for the preparation of paranitrosophenol.

The hydrochloric acid solution will contain diethylammonium chloride, some ethyl aniline regenerated from nitrosoethyl aniline which has distilled over, some diethyl aniline, and probably other substances. Evaporate on the water-bath to about 50 cc., transfer to a 200 cc. flask, cool thoroughly, add, with cooling, 60 cc. of sodium hydroxide (3 cc. = 1 gram), connect the flask by means of a tightly fitting cork, with a glass tube one cm. in diameter and about 60 cm. long, and held in a clamp at an angle of 45° with the perpendicular. About 15 cm. of the upper end of the tube, which serves as a reflex condenser, should be bent downward and this should dip into a flask containing 10 cc. of concentrated hydrochloric acid. If the lower portion of the tube is filled with glass beads a better separation will be effected. Distil very slowly, in such a manner that the ethyl aniline and similar substances almost entirely condense and run back. Sometimes it may be necessary to neutralize the distillate with 50 cc. of sodium hydroxide, and distil again before a pure distillate can be obtained. Finally evaporate the solution of diethylammonium chloride nearly or quite to dryness, transfer to a flask or distilling bulb, decompose with a very concentrated solution of sodium or potassium hydroxide, and distil from the water-bath. To obtain the amine free from water it must be dried with fused caustic potash and distilled again. Yield 7 to 8 grams.

Diethyl amine boils at 55°-56°, and has a specific gravity of 0.7028 at 25°. The hydrochloride melts at 215°-217°, boils at 320°-330°, and is very easily soluble in water, but difficultly soluble in absolute alcohol.

107. Preparation of an Amine from an Oxime.—Isopropyl amine,



$$(CH_3)_2C\begin{matrix}NH_2\\H\end{matrix}$$

. (2-aminopropane.)

Literature.—Sierch: Ann., 148, 263; Gautier: Ann. chim. phys., [4], 17, 251; Hofmann: Ber., 15, 768; Tafel: *Ibid,* 19, 1926; Goldschmidt: *Ibid,* 20, 728; Noyes: Am. Chem. J., 14, 226; 15, 540.

10 grams acetoxime.
20 grams sodium.
240 cc. absolute alcohol.

Put in a 200 cc. round-bottomed flask 20 grams of sodium, connect with a long, reversed condenser, and pour through the latter a solution of 10 grams of acetoxime in 60 cc. of absolute alcohol. By means of a short tube, bent twice at right angles and passing through rubber stoppers, connect the top of the condenser with a U-tube containing 5 to 6 cc. of concentrated hydrochloric acid. Because of the low boiling-point of isopropyl amine this is necessary, but with amines of higher molecular weight it is not required. When the first violent action slackens, warm on an asbestos plate and add from time to time through the condenser, more alcohol, whenever a crust forms on the sodium. About 240 cc. of alcohol will be required. When the sodium has all dissolved, add 40 cc. of water through the condenser, cool, and then distil off the alcohol and isopropyl amine, collecting in a flask containing 12 cc. of concentrated hydrochloric acid, including that from the U-tube. Evaporate to dryness, and preserve the amine in the form of its hydrochloride. Yield 8 to 10 grams.

Isopropyl amine boils at 31.5°, and has an ammoniacal, fishy odor. Its specific gravity is 0.690 at 18°. The hydrochloride is deliquescent and melts at 153°-155°. The chloroplatinate is difficultly soluble, and melts at 227°-228°. The salt is easily prepared by adding chloroplatinic acid, ("platinic chloride"), H_2PtCl_6, to a concentrated solution of the chloride. It can be analyzed by careful ignition in a porcelain crucible.

108. Preparation of an Amine by the Reduction of a Cyanide.—ω-Phenyl-ethyl-amine, $C_6H_5CH_2CH_2NH_2$. (1^2-amino-ethylphen.)

Literature.—Cannizzaro: Ann., 96, 247; Mann: Ber., 14, 1645; Stadel: *Ibid,* 19, 1951; Hotter: *Ibid,* 20, 82; Spica, Columbo: Gaz. chim. Ital., 5, 124; Bernthsen: Ann., 184, 304; Ladenburg: Ber., 18, 2956; 8, 19, 782; Hofmann: *Ibid,* 18, 2740; Hoogewerf, van Dorp: Rec. trav. chim. Pays-Bas., 5, 254; Fileti, Piccini: Ber., 12, 1700.

30 grams benzyl chloride.
38 cc. alcohol.
18 grams potassium cyanide.
17 grams water.

5 grams benzyl cyanide.
6 grams sodium.
70 cc. absolute alcohol.

8 cc. hydrochloric acid (sp. gr. 1.10).

Put in a round-bottomed flask 18 grams of *pure* powdered potassium cyanide, 17 cc. of water, 30 grams of benzyl chloride, and 38 cc. of alcohol. Connect with an upright condenser, and boil on a wire gauze or asbestos plate for 3 to 4 hours. By means of a separatory funnel separate the alcoholic solution, containing the benzyl cyanide, from the lower aqueous layer and distil the former. The alcohol and water may be distilled with advantage from a water-bath under diminished pressure and the heating continued till the residual liquid is dry (see 55, p. 138). In any case the portion boiling at 210°-240° will, if *dry*, be sufficiently pure for this preparation. Yield of benzyl cyanide 20 to 22 grams.

Put in a 200 cc. round-bottomed flask 6 grams of sodium, cut in small pieces, add a warm solution of 5 grams of benzyl cyanide in 30 cc. of absolute alcohol, connect with an upright condenser, and heat rapidly to boiling. Continue to boil and add more alcohol as necessary, in all 70 to 80 cc., till the sodium is dissolved. Distil off the alcohol and the phenylethylamine in a current of steam, distilling as long as the distillate comes over alkaline. Add to the distillate 8 cc. of hydrochloric acid, evaporate to a small volume, filter, and evaporate to dryness. Transfer the residue to a small test-tube, dissolve in 2 to 3 cc. of hot water, cool, add 8 cc. of sodium hydroxide (3 cc. = 1 gram), and a few cc. of ether, and shake vigorously. Allow the ethereal layer to separate, and by means of a pipette with a fine capillary tube, remove as much as possible of the aqueous solution from below. Pour off the ethereal solution into a dry tube, rinse with a little ether, and dry the ethereal solution by adding solid caustic potash and leaving it for 24 hours. Transfer to a small (15 cc. or less) distilling bulb, and distil the ether through a condenser and then the amine directly into a small preparation tube. Yield about 2.5 grams of the hydrochloride, and 1.5 grams of the distilled amine.

This method of reducing cyanides led Ladenburg to the synthesis of cadaverine from trimethylene cyanide,

$$CNCH_2CH_2CH_2CN.$$

With ethylene cyanide and phenyl cyanide it gives less satisfactory results, owing, in the latter case, to secondary reactions which give partly benzene and sodium cyanide and partly sodium benzoate and ammonia.

Benzyl cyanide boils at 231.7°. ω-Phenyl-ethylamine is a colorless liquid which has a slightly ammoniacal odor, and boils at 198°. It has a specific gravity of 0.958 at 24.4°. It is a strong base. It is somewhat soluble in water, and is easily soluble in alcohol and ether. The hydrochloride, $C_6H_5CH_2CH_2NH_2HCl$, crystallizes from absolute alcohol in leaflets or plates, which melt at 217° and dissolve in 1¼ parts of water at 14°. It is less easily soluble in hydrochloric acid, easily soluble in alcohol. The chloroplatinate is difficultly soluble in cold water.

109. **Benzyl Amine.**—$C_6H_5CH_2NH_2$, Aminomethylphen.

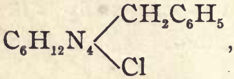
Literature.—Mendius: Ann., **121**, 144; Bamberger, Ladter: Ber., **20**, 1709; Cannizzaro: Ann., **134**, 128; Hofmann: Ber., **18**, 2738; Tafel: *Ibid*, **19**, 1928; Curtius, Lederer: *Ibid*, **19**, 2463; Leuckhart, Bach: *Ibid*, **19**, 2128; Goldschmidt: *Ibid*, **19**, 3232; Mason: J. Chem. Soc., **63**, 1313; Seelig: Ber., **23**, 2971; Hoogewerf, van Dorp: Rec. trav. chim. Pays-Bas., **5**, 253; Delepine: Compt. rend., **120**, 501; **124**, 292.

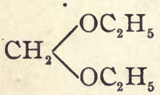
50 cc. formaldehyde solution (40 per cent.).
50 cc. ammonia (sp. gr. 0.90).

10 grams hexamethylene amine.
10 grams benzyl chloride.
30 cc. chloroform.

16 grams double compound of hexamethylene amine with benzyl chloride.
45 cc. alcohol.
15 cc. concentrated hydrochloric acid.

Put in a 150 cc. distilling bulb 50 cc. of a 40 per cent. solution of formaldehyde and add in small portions, cooling somewhat, 50 cc. of ammonium hydroxide (0.90). Heat for 5 to 10 minutes on a water-bath, put in the mouth of the bulb a rubber stopper bearing a fine capillary tube (see 75, p. 171), and distil as rapidly as possible from the water-bath, under diminished pressure, till the residue of hexamethylene amine appears dry. Rinse out the amine with a mixture of two volumes of ether with one volume of alcohol and suck off on a Witt plate. Wash with a little ether and dry on the water-bath. 10 grams of the amine should be obtained. A small additional quantity of amine may be obtained from the alcohol-ether mother-liquors.

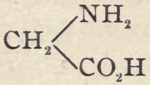
Put in a small flask 10 grams of the hexamethylene amine, 30 cc. of chloroform, and 10 grams of benzyl chloride. Connect with an upright condenser, and boil gently on a water-bath for half an hour. Allow to cool, filter, and wash with a little chloroform. About 16 grams of the double compound,  $C_6H_{12}N_4\begin{cases}CH_2C_6H_5\\Cl\end{cases}$, should be obtained. An additional small amount of the compound will separate from the mother-liquors on standing.

Put in a distilling bulb 16 grams of the double compound last mentioned, and 60 cc. of a mixture of three volumes of alcohol and one volume of concentrated hydrochloric acid. Connect with an upright condenser, and heat on a water-bath for an hour, then distil from the water-bath the methylenediethyl ether,  $CH_2\begin{cases}OC_2H_5\\OC_2H_5\end{cases}$, which has been formed. Add to the residue 20 cc. of the same mixture of alcohol and hydrochloric acid, and heat again for an hour on the water-bath, allowing the methylenediethyl ether to distil through a condenser as it is formed. Then distil over a free flame till 20 to 25 cc. in all have passed over. Repeat this process a second time, and, if necessary, a third, or till the odor of the ether can no longer be detected in the distillate. The complete decomposition of the double compound is essential to the success of the preparation.

Transfer the residue in the bulb to an evaporating dish, and evaporate on the water-bath nearly or quite to dryness. Transfer the residue to a flask, add a strong solution of sodium hydroxide in considerable excess, separate the benzyl amine by means of a separatory funnel, dry it by allowing it to stand with solid caustic potash, and distil. Yield 4 to 5 grams. In working with larger quantities the yield is somewhat better.

The methylenediethyl ether, which is formed as a by-product, boils at 89°, and has a specific gravity of 0.851 at 0°. It dissolves in 11 volumes of water at 18°.

Benzyl amine boils at 183°, and has a specific gravity of 0.9826 at $\frac{18.9^\circ}{4^\circ}$. It is miscible in all proportions with water, alcohol, and ether, but is separated from aqueous solutions on the addition of sodium hydroxide. It has a strong alkaline reaction, and absorbs carbon dioxide from the air.

110. Preparation of an Amino Acid from a Halogen Derivative of an Acid.—Glycocoll,  $CH_2\begin{cases}NH_2\\CO_2H\end{cases}$. (Aminoethanoic acid.)

Literature.—Braconnot. Ann. chim. phys., 1820, 13, 114; Perkin, Duppa: Ann., 108, 112; Heintz: *Ibid,* 122, 257; 124, 297; v. Nencki: Ber., 16, 2827; Kraut: Ann., 266, 295; Ber., 23, 2577; Gabriel, Kroseberg: *Ibid,* 22, 427.

25 grams monochloracetic acid.
25 cc. water.
300 cc. ammonium hydroxide (sp. gr. 0.90).

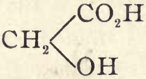
To 300 cc. of ammonia (0.90) in a liter flask or distilling bulb, add a solution of 25 grams of monochloracetic acid in 25 cc. of water. After thorough shaking, allow the whole to stand for 24 hours. Distil off most of the excess of ammonia with water vapor (see **22**, p. 71), and evaporate the solution on the water-bath till the odor of ammonia is no longer apparent. Add to the solution the copper oxide prepared from 35 grams of copper sulphate by precipitating from a hot solution with sodium hydroxide, and washing twice by decantation. Boil, filter, evaporate, and crystallize the copper aminoacetate which is formed.

To prepare the free glycocoll, dissolve the copper salt in water, add a little freshly precipitated and slightly washed aluminium hydroxide, precipitate with hydrogen sulphide, boil a few minutes, filter, and wash with water containing a little hydrogen sulphide. Evaporate the filtrate to a small volume and allow the glycocoll to crystallize.

In case the glycocoll contains an ammonium compound, warm the concentrated solution with milk of lime until the odor of ammonia disappears, filter, precipitate the calcium with ammonium carbonate, filter, and crystallize.

The addition of the aluminium hydroxide prevents the formation of a colloidal solution of the copper sulphide which is difficult to filter.

Yield 5 to 8 grams. The yield is very considerably below the theoretical, because of the formation of the secondary and tertiary amino acetic acid, $NH(CH_2CO_2H)_2$ and $N(CH_2CO_2H)_3$. The large excess of ammonia, and the quick mixing of the chloracetic acid with the ammonia, after it has been added, tend to increase the amount of the primary compound, which is desired.

Glycocoll crystallizes in monoclinic crystals, which turn brown at 228°, and melt at 232°-236°. It is soluble in 4.3 parts of cold water, in 930 parts of alcohol of 0.828 sp. gr., and insoluble in absolute alcohol. Its neutral solution gives a deep red color with ferric chloride. It forms crystalline salts with nitric and with hydrochloric acid. When distilled with barium hydroxide it gives methyl amine and barium carbonate. With nitrous acid it gives glycollic acid,  $CH_2\left\langle\begin{matrix}CO_2H\\OH\end{matrix}\right.$.

111. Preparation of an Acyl Derivative of an Amino Acid.—Hippuric acid, $C_6H_5CONHCH_2CO_2H$. (Benzoyl aminoacetic acid).

Literature.—Occurrence in urine of cattle, Kraut: Jahresb., 1858, 573; Henneberg, Stohmann and Rautenberg: Ann., 124, 200; In human urine, Hallwachs: Ann., 106, 164; In urine of persons who have taken benzoic acid, Herter; Report on use of benzoic acid as a preservative, C. A., 1910, 2690; Preparation, Baum: Ber., 19, 502; From urine of the horse or cow, Gregory: Ann., 63, 125.

2.5 grams aminoacetic acid.
30 cc. sodium hydroxide (10 per cent.).
4.5 grams benzoyl chloride.

Dissolve 2.5 grams (1/30 mol.) of glycocoll[1] in 30 cc. of a ten per cent. solution of sodium hydroxide, add 4.5 grams (1/30 mol.) of benzoyl chloride and shake till the odor of the chloride disappears. Filter, if the solution is not clear, and precipitate the hippuric acid with a slight excess of hydrochloric acid. Recrystallize from hot water.

[1] Instead of free glycocoll the necessary amount of the copper salt may be dissolved in water and the copper precipitated as directed on p. 231. The filtrate from the copper sulphide may then be evaporated to a small volume and the solution used as directed.

Hippuric acid crystallizes in thick needles which melt at 187.5°. The preparation of hippuric acid here given is closely related to the preparation of polypeptides by Fischer and the formation of hippuric acid in the animal organism is very probably related to the synthesis of proteins in the processes of life.

112. Preparation of an α-Amino Acid Through the Aminonitrile.—α-Aminoisobutyric acid, $(CH_3)_2CHNH_2CO_2H$.

Literature.—Urech: Ann., 164, 268; Tiemann, Friedländer: Ber., 14, 1971; Zelinsky, Stadnikoff: Ber., 39, 1726.

13 grams potassium cyanide.
10.6 grams ammonium chloride.
Water to dissolve each.

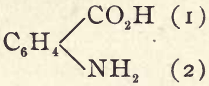
11.6 grams acetone.

Concentrated hydrochloric acid.

Dissolve separately 13 grams (⅕ mol.) potassium cyanide and 10.6 grams (⅕ mol.) of ammonium chloride in two small flasks. Put the solution of ammonium chloride into a 100 cc. strong, glass stoppered bottle, add 11.6 grams (⅕ mol.) of acetone, then the solution of potassium cyanide, insert the stopper, mix quickly and tie the stopper down by means of a piece of cloth placed over the top and tied tightly around the neck of the bottle. Allow the mixture to stand in a warm place (40°-50°) over night. Transfer the solution to a strong, round-bottomed flask and add (*under the hood*) an equal volume of concentrated hydrochloric acid. Connect with an upright condenser and boil for two hours. Pour the solution into an evaporating dish and evaporate to dryness either on the water-bath or on an asbestos plate, but in the latter case care must be taken that the residue is not overheated. Transfer the residue to a flask and extract it repeatedly with a mixture of 10 parts of alcohol with one of ether, which will dissolve the hydrochloride of the amino acid but will leave the inorganic salts undissolved.

Distil off the alcohol and ether, dissolve the hydrochloride of the amino acid in a small amount of water, add twice the theoretical amount of lead carbonate and warm on the water-bath till effervescence ceases. Cool thoroughly, filter on a plate and suck as dry as possible, moisten once with a very little water and suck off again. Remove the lead contained in the filtrate by means of hydrogen sulphide, and evaporate the filtrate till the amino acid crystallizes. Yield 15 grams.

α-Aminoisobutyric acid crystallizes in plates which sublime at 280°-281° without melting. It is very easily soluble in water, difficultly soluble in alcohol, insoluble in ether.

113. Preparation of an Amino Acid from the Half Amide of a Bibasic Acid.—Anthranilic acid,  $C_6H_4\left\langle\begin{array}{ll} CO_2H & (1) \\ NH_2 & (2) \end{array}\right.$ (2-Aminobenzoic acid).

Literature.—Laurent: Jahresb., 1847-48, 589; Ann., 39, 91; Kuhara: Am. Chem. J., 3, 29; Aschan: Ber., 19, 1402; Fritzsche: Ann., 39, 83; Beilstein, Kuhlberg: *Ibid*, 163, 138; Bedson: J. Chem. Soc., 37, 752, (*1880*); Hoogewerf, van Dorp: Rec. trav. chim. Pays-Bas., 10, 6, Marignac: Ann., 42, 215.

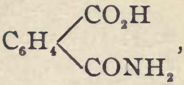
20 grams phthalic anhydride.
80 cc. ammonia (0.96).

64 cc. hydrochloric acid (1.112).

16.5 grams phthalamidic acid.
100 cc. sodium hydroxide, (10 per cent.).

140 cc. sodium hydroxide (10 per cent.).
16 grams bromine (5.1 cc.).

35 cc. hydrochloric acid (1.112).
40 cc. acetic acid (30 per cent.).

Add 20 grams of finely powdered phthalic anhydride in portions to 80 cc. of ammonia (sp. gr. 0.96—not stronger—as strong ammonia may cause the formation of phthalimide) in a 200 cc. flask, shaking and cooling the mixture. When the anhydride is nearly dissolved filter and to the filtrate add 64 cc. of hydrochloric acid (4 cc. = 1 gram), cool again thoroughly with shaking, filter off on a plate, stop the pump, moisten with water, suck off and repeat once. Dry the phthalamidic acid,  $C_6H_4\left<\begin{matrix}CO_2H\\CONH_2\end{matrix}\right.$, on filter-paper in the air, or, better, *in vacuo* over sulphuric acid. The yield should be about 20 grams.

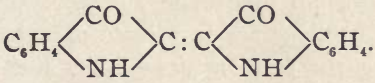
Put 140 cc. of a ten per cent. solution of sodium hydroxide in a flask, add from a burette 16 grams (5.1 cc = 1 mol.) of bromine, and dissolve it immediately by giving the flask a quick rotary motion.[1] Dissolve 16.5 grams (1 mol.) of phthalamidic acid in 100 cc. of ten per cent. sodium hydroxide, and add the solution of sodium hypobromite in portions of about 20 cc. at intervals of one to two minutes, cooling after each addition. Neither solution should stand but a few minutes before use. Allow the mixture to stand for half an hour, add a little of a strong solution of acid sodium sulphite to reduce the excess of sodium hypobromite, and 35 cc. of hydrochloric acid (4 cc. = 1 gram), carefully, on account of the effervescence. Evaporate to about 100 cc. Filter, if necessary and add 40 cc. of acetic acid (30 per cent.). Filter off the anthranilic acid after cooling, suck it as free as possible of the mother-liquors and recrystallize from hot water. Yield 10 to 11 grams.

For a discussion of the reactions involved in the transformation of the amide group into an amino group with loss of carbonyl see p. 219.

Anthranilic acid crystallizes in leaflets which melt at 144°-145°. It is easily soluble in water. The aqueous solution shows a blue fluorescence and tastes sweet.

The preparation of anthranilic acid from indigo is of especial historic interest. The acid may also be prepared by the reduction of orthonitrobenzoic acid.

114. Preparation of Indigo from Anthranilic Acid,



$C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>C:C\left<\begin{matrix}CO\\NH\end{matrix}\right>C_6H_4$.

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[1] A hypobromite solution more nearly free from bromate may be prepared by putting the bromine in a glass-stoppered wash-bottle, set in warm water and aspirating the vapor of the bromine into the solution of sodium hydroxide contained in two wash-bottles set in cold water.

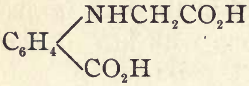
Literature.—Baeyer's synthesis of indigo: Ber., 11, 1228, 1296; 13, 2254; Heumann's synthesis: Ber., 23, 3431; Mauthner and Suida: Monatsh, 9, 728; History of the synthesis of indigo, Baeyer: Ber., 33, LI; Brunck: Ber., 33, LXXI; Henle: Anleit. zur org. präp. Prakticum, p. 63.

6.8 grams anthranilic acid.
5.7 grams chloracetic acid.
8.5 grams dry sodium carbonate.
50 cc. water.

Hydrochloric acid.

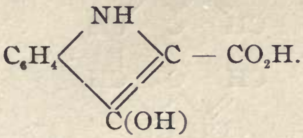
4 grams phenylglycine-*o*-carboxylic acid.
17 cc. sodium hydroxide (10 per cent.).

10 grams sodium hydroxide.
10 grams potassium hydroxide.

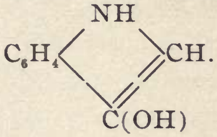
Put 6.8 grams of anthranilic acid, 5.7 grams of chloracetic acid, 8.5 grams of dry sodium carbonate and 50 cc. of water in a 200 cc. flask, connect with an upright condenser and boil for 2 to 3 hours. Cool, add hydrochloric acid in slight excess, filter off the precipitated phenylglycine-*o*-carboxylic acid,  $C_6H_4\left\langle\begin{array}{l}NHCH_2CO_2H\\CO_2H\end{array}\right.$, after standing for some hours and recrystallize it from water.

Dissolve 4 grams of the phenylglycine-*o*-carboxylic acid in 17 cc. of sodium hydroxide (10 per cent.), evaporate the solution to dryness on the water-bath and dry the powdered residue at 140°.

In a not too small nickel crucible melt 10 grams of sodium hydroxide and 10 grams of potassium hydroxide and heat till the water is expelled and the hydroxides are in a state of quiet fusion. Cool to 270°, measuring the temperature with a thermometer enclosed in a copper or iron tube, closed below. Add the sodium salt previously prepared, stir and keep the mixture at 260°-270° for ten or fifteen minutes. This treatment causes the condensation of the acid to indoxylic acid,

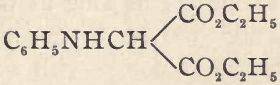


When the mass is cold, dissolve it in 50 cc. of water and boil gently for half an hour. This causes the loss of carbon dioxide and conversion of the indoxylic acid to indoxyl,



Add 100 cc. of water and draw or blow a rapid current of air through the solution for several hours. This will cause the oxidation and condensation of two molecules of indoxyl to one of indigo. Yield about 1 gram.

115. Preparation of a Complex Secondary Amine from a Primary Amine and a Bromine Derivative of an Ester.—Anilinomalonic ester,



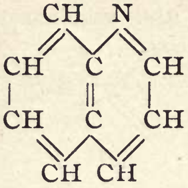
$$C_6H_5NHCH\begin{cases}CO_2C_2H_5\\CO_2C_2H_5\end{cases}.$$

Literature.—Curtiss: Am. Chem. J., 19, 691.

11.95 grams ethyl ester of bromomalonic acid.
9.3 grams aniline.

Put in a small flask 11.95 grams (0.05 mol.) of the ethyl ester of bromomalonic acid and 9.3 grams (0.1 mol.) of aniline. Allow the mixture to stand over night and then complete the reaction by warming for half an hour on the water-bath. Cool, add ether gradually to precipitate the aniline hydrobromide and dissolve the ester. Filter from the hydrobromide, wash the ethereal solution in a separatory funnel two or three times with 5 per cent. sulphuric acid to remove aniline and once or twice with water. Dry the solution with fused potassium carbonate, and evaporate the ether to crystallization. The ester may be purified by recrystallization from alcohol. It crystallizes in needles which melt at 44°-45°. Yield almost quantitative.

116. Skraup's Synthesis of Quinoline.—



Literature.—Gerhardt: Ann., 42, 310; 44, 279; Baeyer: Ber., 12, 460, 1320; Königs: *Ibid,* 12, 453; 13, 911; Wyschnegradsky: *Ibid,* 12, 1480; Skraup, Monatshefte, 1, 317; 2, 141; J. Walter: J. prakt. Chem., 49, 549; Knueppel: Ber., 29, 703; Marckwald: Ann., 279, 3.

24 grams nitrobenzene.
38 grams aniline.
100 grams concentrated sulphuric acid.
120 grams glycerol.

Put in a liter flask the mixture given above, connect with a wide upright condenser, warm slowly till the reaction just begins,[1] remove the flame quickly till it moderates, and then boil for two hours. Cool somewhat, add 100 cc. of water, and distil in a current of steam (see 22, p. 71) as long as the distillate smells of nitrobenzene. Cool, add 300 cc. of caustic soda (3 cc. = 1 gram), and distil over the quinoline with a current of steam. To destroy the aniline which is present, add to the distillate 50 cc. of concentrated hydrochloric acid, and then a strong solution of sodium nitrite, till the solution smells of nitrous acid. Heat to boiling till the diazonium compound is decomposed; add 100 cc. of caustic soda, and distil the quinoline again with water vapor. Collect the quinoline with a little ether, distil off the ether, dry the residue with solid caustic potash, pour off, and distil. Yield about 40 grams.

Quinoline boils at 237°. It gives an orange-yellow, difficultly soluble precipitate with chloroplatinic acid, $(C_9H_7N)_2H_2PtCl_6$.

The nitrobenzene used in the synthesis acts as an oxidizing agent, and Knueppel has shown that it may be replaced with advantage by arsenic acid. The reaction is ,

$$C_6H_5NH_2 + C_3H_8O_3 + O = C_9H_7N + 4H_2O.$$

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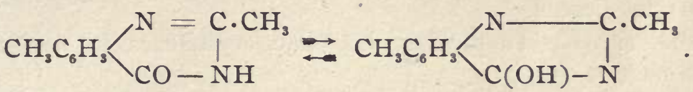
[1] If this operation is conducted carelessly the reaction may become explosively violent.

The same reaction may be applied to a great many derivatives of benzene, naphthalene and anthracene.

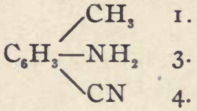
117. Preparation of a Quinazoline from an Acyl Anthranilic Nitrile.—2.7-Dimethyl-4-ketodihydroquinazoline or 2.7-Dimethyl-4-hydroxyquinazoline.



Literature.—General discussion of quinazolines, Bogert: J. Am. Chem. Soc., 32, 784; Preparation of Dimethyl-ketodihydroquinazoline, Bogert and Hoffman: J. Am. Chem. Soc., 27, 1296, 1299.

4 grams homoanthranilic nitrile.
5 cc. acetic anhydride.

1.5 grams acetyl homoanthranilic nitrile.
50 cc. potassium hydroxide (10 per cent.).
50 cc. hydrogen peroxide (3 per cent.).

Put 4 grams of homoanthranilic nitrile,[1]  $C_6H_3\begin{array}{l} \diagup CH_3 \quad 1. \\ -NH_2 \quad 3. \\ \diagdown CN \quad 4. \end{array}$, and 5 cc. of acetic anhydride in a long test-tube and boil gently with a micro burner for two hours, covering the mouth of the tube with a small watch-glass and taking care not to boil so vigorously that the anhydride escapes. Pour the solution into water and crystallize the acetyl homoanthranilic nitrile from dilute acetic acid and from alcohol. It crystallizes in colorless needles, which melt at 136°.

Put 1.5 grams of acetyl homoanthranilic nitrile in a 150 cc. flask, add 50 cc. of a 10 per cent. solution of potassium hydroxide and 50 cc. of a 3 per cent. ("10 volume") solution of hydrogen peroxide and warm at 40°-50° for two hours. The alkaline

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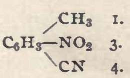
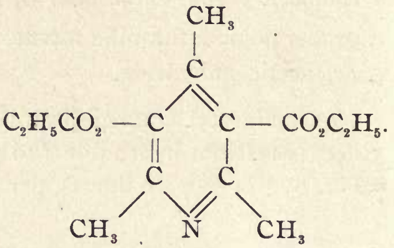
[1] The nitro nitrile,  $C_6H_3\begin{array}{l} \diagup CH_3 \quad 1. \\ -NO_2 \quad 3. \\ \diagdown CN \quad 4. \end{array}$, may be prepared by Sandmeyer's reaction (p. 131) from *m*-nitro-*p*-toluidine (p. 213) (see Bogert and Hoffman, J. Am. Chem. Soc., 27, 1294 Bogert and Hand, *Ibid*, (24, 1035) Noyes, Am. Chem. J., 10, 477). The nitro-nitrile is reduced to the amino-nitrile by stannous chloride and hydrochloric acid (Bogert and Hoffman, J. Am. Chem. Soc., 27, 1295).

hydrogen peroxide solution saponifies the nitrile to the amide and the latter condenses to form the quinazoline. The latter dissolves either in strong acids or in strong bases (why)? Add 10 cc. of concentrated hydrochloric acid (1.19) and then a slight excess of ammonia. Crystallize the precipitated quinazoline from alcohol.

2.7-Dimethyl-4-ketodihydroquinazoline crystallizes in needles which melt at 255°.

118. Preparation of a Derivative of Pyridine by Condensation.

– Collidinedicarboxyllic ester,



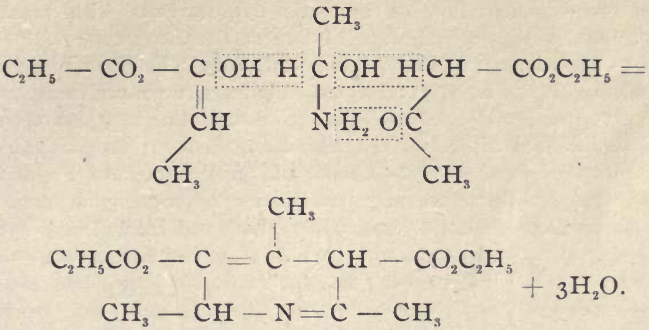
Literature.—Hantsch: Ann., 215, 8; Michael: *Ibid,* 225, 123; Bamberger: Ber., 24, 1763.

20 grams acetoacetic ester.
5 grams aldehyde ammonia.
10 grams dihydrocollidinedicarboxyllic ester.

Arsenious anhydride.
Nitric acid (sp. gr. 1.30-1.33).

Put in a small beaker 20 grams of acetoacetic ester, and add five grams of aldehyde ammonia. Warm gently till the reaction begins, remove the flame for a short time, and then boil, with stirring, for four or five minutes in all. Add a little alcohol, and allow to cool till the dihydrocollidinedicarboxyllic ester crystallizes; filter, wash once with dilute alcohol, and then with water. A small amount of less pure ester may be obtained by diluting the filtrate.

The reaction takes place in some such manner as the following:

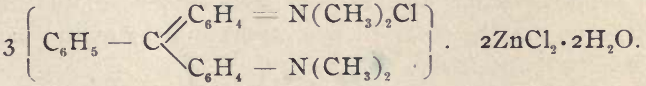


Put 10 grams of the crude ester in a small flask, add 20 cc. of alcohol, and pass in a rapid stream of the oxides of nitrogen, generated by warming arsenious oxide with nitric acid of sp. gr. 1.30-1.33, passing the gases through an empty Drechsel wash-bottle to condense water. Rubber connections must be avoided as far as possible, because the gas attacks them. Continue the passage of the gas till a drop of the solution dissolves clear in dilute hydrochloric acid. Evaporate the alcohol on the water-bath, add a strong solution of sodium carbonate, and take up the collidinedicarboxyllic ester with ether. Dry the ethereal solution with ignited potassium carbonate, and distil from a small distilling bulb. Yield 7 to 8 grams.

The dihydro ester crystallizes in colorless plates, which melt at 131°. Its solutions show a beautiful blue fluorescence. It is almost insoluble in water, and in dilute acids, difficultly soluble in cold alcohol, easily soluble in hot alcohol, and in chloroform. It dissolves in concentrated hydrochloric or sulphuric acid.

Collidinedicarboxyllic diethyl ester boils at 308°-310°. It is easily saponified by alcoholic potash, giving a potassium salt difficultly soluble in alcohol. Collidine may be obtained from this potassium salt by mixing it with calcium hydroxide and distilling.

119. Preparation of a Leuco Base and Dye by Condensation of an Aldehyde with an Aromatic Amine.—Malachite Green.

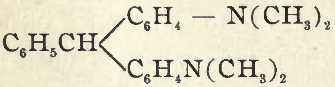


Literature.—Condensation of aromatic hydrocarbons with aldehydes, Baeyer: Ber., 6, 963; Preparation of Leucomalachite green, O. Fischer: Ann., 206, 83, 122, 129; Döbner: Ann., 217, 250-253; E. Fischer: Anleiting z. Darst, org. Präparte, p. 71; Henle: Anleitung zur anorg. präp. prakticum p. 153; Preparation and constitution of rosaniline and pararosaniline, O. and E. Fischer: Ann., 194, 242, 285; Ber., 11, 1079; 13, 2204; Crystal-violet, Hofmann: Ber., 18, 767; Carbinol and quinoid formulæ, Friedländer: Ber., 26, 173; Nomenclature and classification of triphenylmethane dyes, Baeyer and Villiger: Ber., 37, 597, 2848; Theory of colored and colorless compounds, Hantsch: Ber., 33, 278, 752; 38, 2143; Gomberg: Ber., 40, 1868, 1875; Baeyer and Villiger: Ber., 37, 597, 2848; 38, 569; Ann., 354, 152; Wilstätter: Ber., 41, 1458; Curtiss: J. Am. Chem. Soc., 32, 795; Isorrepsis, Baly and Stewart: J. Chem. Soc., 89, 498, 513; Development of the coal tar dyes, Caro: Ber., 25, R. 955.

12 grams dimethyl aniline.
5 grams benzaldehyde.
10 grams fused zinc chloride.

3.3 grams leuco base.
40 cc. normal hydrochloric acid.
2.4 grams lead peroxide.
3.5 grams zinc chloride.
Saturated solution of salt.

Put 12 grams of dimethylaniline, 5 grams of benzaldehyde and 10 grams of fused zinc chloride in a porcelain dish and warm on a water-bath for some hours, stirring occasionally and adding a few drops of water if the mixture becomes too viscous. Transfer the mixture to a flask or distilling bulb and drive out the excess of dimethyl aniline with a current of steam. Cool, pour off the aqueous solution of zinc chloride, dissolve the leuco base, tetramethyldiaminotriphenylmethane,



$$C_6H_5CH\left\langle\begin{array}{l}C_6H_4-N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}\right.$$

, in a considerable amount of hot alcohol, filter, if the solution is not clear, and allow to crystallize. If the base separates as an oil at first, dissolve again in more alcohol. After the crystals have been separated an additional crop may be obtained by evaporating the mother-liquors. The base melts at 102°.

Dissolve 3.3 grams of the leuco compound in 40 cc. of hot, normal hydrochloric acid, dilute with 300 cc. of water and add gradually, with vigorous shaking, 2.4 grams of lead peroxide mixed with about 20 cc. of water[1]. Shake vigorously for about 10 minutes in all. Add an aqueous solution of 3.5 grams of zinc chloride and then, gradually, a saturated solution of salt until a portion of the mixture gives a colorless filtrate. Filter and wash once with a salt solution. Dissolve the compound in hot water and reprecipitate again with a saturated salt solution.

Dissolve a little of the malachite green in strong hydrochloric acid and note the effect of dilution with water. Dissolve some of the dye in water and add ammonia, then dilute hydrochloric acid. Reduce some of the substance to the leuco base by means of zinc and dilute hydrochloric acid. See Döbner: Ann., **217**, 251 and 252.

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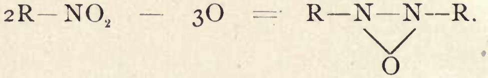
[1] The per cent. of pure lead peroxide in the reagent must be known and enough taken to give 2.4 grams of the pure compound.

Chapter XIV

DIAZO, HYDRAZO, NITROSO AND OTHER NITROGEN COMPOUNDS

A considerable number of other nitrogen compounds beside amines and nitro derivatives are known. Most of these are obtained by reduction of nitro compounds, by oxidation of amines, or by condensations with the use of the compounds resulting from such reduction or oxidation. Unless otherwise stated, the following methods apply to the aromatic series only. In some cases similar derivatives of the marsh gas series are known, but usually they require different methods of preparation.

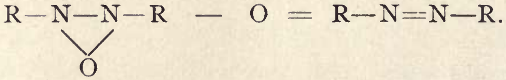
Azoxy compounds are formed by boiling nitro compounds with a solution of caustic potash in methyl or ethyl alcohol, or with a solution of sodium ethylate, or methylate, the alcohol acting as the reducing agent.



$$2R-NO_2 \;-\; 3O \;=\; R-\underset{\underset{O}{\vee}}{N-N}-R.$$

The method cannot be applied to compounds having a methyl group para to the nitro group, because condensation to derivatives of dibenzyl, $C_6H_5CH_2CH_2C_6H_5$, or stilbene, $C_6H_5CH = CHC_6H_5$, takes place.

Azo compounds are prepared by the reduction of azoxy compounds by distillation with iron filings, by the direct reduction of nitro compounds with zinc dust and alcoholic potash, or by the oxidation of hydrazo compounds by means of the oxygen of the air acting on a solution in alcohol containing a little alkali.



$$R-\underset{\underset{O}{\vee}}{N-N}-R \;-\; O \;=\; R-N=N-R.$$

$$2R-NO_2 \;-\; 4O \;=\; R-N=N-R.$$

$$R-NH-NH-R + O \;=\; R-N=N-R + H_2O.$$

Aminoazo, $R-N=N-R-NH_2$, and hydroxyazo (usually called in German text-books "oxyazo"), R—N=N—R—OH, compounds are formed by the condensation of diazonium compounds, with amines or phenols. As the condensation takes place usually in neutral, or slightly acid solutions, but does, not. as a rule, occur in either strongly alkaline or strongly acid solutions, Bamberger supposes the reaction to take place between the diazonium hydroxide and the other compound. (Ber., 28, 444.)

$$R—N=N—OH + H—R—NH_2 = R—N=N—R—NH_2 + H_2O.$$

This kind of condensation takes place most readily with tertiary amines, and with primary metadiamines. Primary and secondary amines, on the other hand, condense in acetic acid solutions, with the formation of diazoamino compounds.

$$R—N=N—OH + R—NH_2 = R—N=N—NHR + H_2O.$$

These diazoamino compounds, when allowed to stand with cold dilute hydrochloric acid, or when warmed with the hydrochloride of the amine, dissolved in the free amine, usually pass over into the corresponding aminoazo compound; *e.g.*:

$$\underset{\text{Diazoamino benzene}}{C_6H_5—N=N—NHC_6H_5} \rightarrow \underset{\text{Aminoazobenzene}}{C_6H_5—N=N—C_6H_4NH_2}.$$

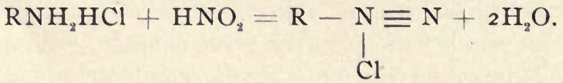
This combination ("Kuppelung") of diazonium compounds with amines and phenols, and the transformation of diazoamino into aminoazo compounds, are of great technical importance. O. N. Witt has pointed out that dye-stuffs must have two characteristics; they must have a color group ("chromophore"), *e.g.*, the azo, or nitro group, and they must also have a salt-forming group, ("auxochrome"), *e.g.*, hydroxyl, or the amino group, which will enable the substance to combine with the fiber in dyeing. The azo compounds are all of them colored, but only those of them which contain some "auxochrome" group as well can be used in dyeing.

All organic coloring matters are changed to colorless compounds by reduction. These colorless compounds have received the general name of "leuco" compounds (see p. 241 also) ("Leukoverbindungen," from Greek λευκος, white). The leuco compounds corresponding to the azo compounds are the hydrazo compounds. These may be prepared from the azo compounds by reduction with alcoholic ammonium sulphide, or with zinc dust and alcoholic potash or soda. They may also be prepared by direct reduction of nitro compounds with zinc dust and alcoholic potash.

$$R-N=N-R + 2H = R-NH-NH-R.$$

$$2R-NO_2 + 10H = R-NH-NH-R + 4H_2O.$$

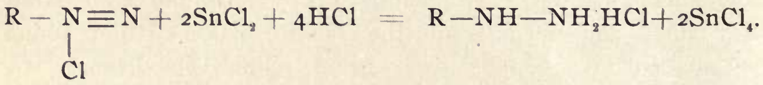
Diazonium compounds are formed by the action of nitrous acid on amines in acid solutions.



$$RNH_2HCl + HNO_2 = R - \underset{\underset{Cl}{|}}{N} \equiv N + 2H_2O.$$

On account of their instability, diazonium compounds are not usually separated, but are used for synthetical purposes immediately after preparation. Several illustrations of such use have already been given. (See pp. 702, 131, 201.)

Hydrazines are prepared by the reduction of diazonium compounds with stannous chloride, with acid sodium sulphite, or with acid sodium sulphite, zinc dust and acetic acid, followed by the decomposition of the resulting sulphonic acid with hydrochloric acid.



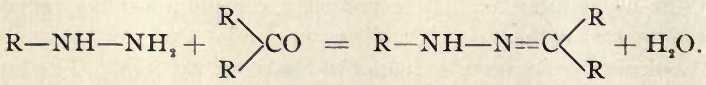
$$R - \underset{\underset{Cl}{|}}{N} \equiv N + 2SnCl_2 + 4HCl = R-NH-NH_2HCl + 2SnCl_4.$$

$$R - \underset{\underset{Cl}{|}}{N} \equiv N + HNaSO_3 = R-N=N-SO_3Na + HCl.$$

$$R-N=N-SO_3Na + 2H = R-NH-NH-SO_3Na.$$

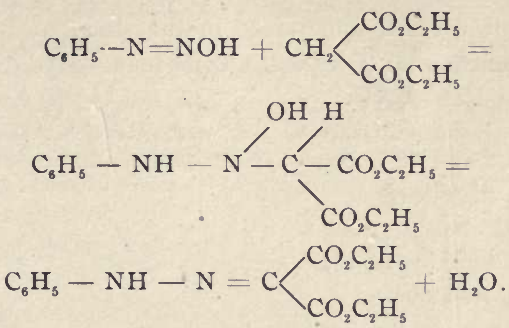
$$R-NH-NH-SO_3Na + HCl + H_2O = R-NH-NH_2HCl + NaHSO_4.$$

Hydrazones are formed by the condensation of hydrazines with aldehydes or ketones, usually in neutral or acetic acid solution.



$$R-NH-NH_2 + \begin{matrix}R\\R\end{matrix}\!\!>CO = R-NH-N=C\!\!<\!\begin{matrix}R\\R\end{matrix} + H_2O.$$

Hydrazones are also formed by the condensation of diazonium compounds with substances containing a methylene group between two carboxyl groups. Owing to a different view of the structure of these compounds, which prevailed before they had been fully studied, they are frequently called azo compounds.

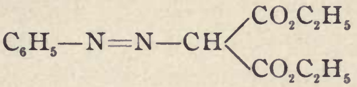


$$C_6H_5-N=NOH + CH_2\left\langle\begin{array}{l}CO_2C_2H_5\\CO_2C_2H_5\end{array}\right. =$$

$$C_6H_5 - NH - \overset{OH}{N} - \overset{H}{C}\begin{array}{l}- CO_2C_2H_5 =\\ \diagdown CO_2C_2H_5\end{array}$$

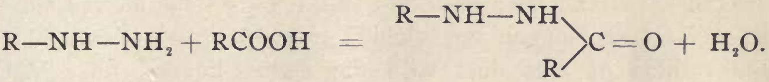
$$C_6H_5 - NH - N = C\left\langle\begin{array}{l}CO_2C_2H_5\\CO_2C_2H_5\end{array}\right. + H_2O.$$

Hydrazone of mesoxalic acid



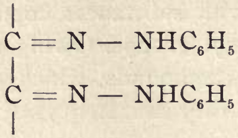
On the supposition that the structure was represented by the formula $C_6H_5-N=N-CH\left\langle\begin{array}{l}CO_2C_2H_5\\CO_2C_2H_5\end{array}\right.$, this was called benzenazomalonic ester, a name still used.

Hydrazides are formed by the condensation of hydrazines, with compounds containing hydroxyl, the condensation taking place readily only when the hydroxyl is more or less acid in its properties.



$$R-NH-NH_2 + RCOOH = \left.\begin{array}{r}R-NH-NH\\R\end{array}\right\rangle C=O + H_2O.$$

The name is given from the analogy with amides.

Osazones are formed by the action of an excess of phenyl hydrazine on substances containing the group $\begin{array}{l}|\\CHOH\\|\\CO\\|\end{array}$. A part of the phenyl hydrazine combines at once to form a hydrazone, a second part oxidizes the alcoholic group to a ketonic or aldehyde group, and the latter reacts with more of the hydrazine, giving finally the group, 

$$\begin{array}{l} | \\ C = N - NHC_6H_5 \\ | \\ C = N - NHC_6H_5 \\ | \end{array}$$

. The osazones have been of especial importance in the study of sugars.

120. Preparation of a Hydrazo Compound.—Hydrazobenzene, $C_6H_5—NH—NH—C_6H_5$.

Literature.—Hofmann: Jahresb., *1863*, 424; Alexejew: Ztschr. Chem., *1867*, 33; *1868*, 497; E. Erdmann: Ztschr. angew. Chem., *1893*, 163.

30 grams nitrobenzene.
200 cc. alcohol.
40 cc. sodium hydroxide (3 cc. = 1 gram).
45 grams zinc dust.

Put in a 500 cc. flask 200 cc. of alcohol, 30 grams of nitrobenzene, and 40 cc. of a solution of caustic soda (3 cc = 1 gram). Heat on a water-bath to about 75°, putting in the mouth of the flask a cork bearing a tube to act as an air condenser. Add a small amount of zinc dust, shake and add more, in small portions, till the reaction begins. If the action becomes violent, check it by dipping the flask in cold water. Continue the warming and addition of zinc dust till the solution becomes nearly colorless. Filter hot on a plate, cool quickly, filter off the hydrazobenzene as rapidly as possible, wash with a little alcohol, transfer it to a flask and add at once some alcohol containing a little ammonium sulphide to prevent oxidation. Boil the residue of zinc dust with the mother-liquors, filter and separate the hydrazobenzene as before, and repeat a third time. Then recrystallize the whole from hot alcohol containing ammonium sulphide,. working as rapidly as possible, to prevent oxidation, and finally dry the product in a vacuum desiccator, over sulphuric acid. In recrystallizing, water may be added to the hot, filtered alcoholic solution till it begins to be turbid, to cause the more complete separation of the hydrazobenzene, and the product may be washed with dilute, instead of pure alcohol. It may also be crystallized from ligroïn. Yield 19 to 20 grams.

Hydrazobenzene crystallizes in colorless leaflets, which melt at 131°. It is easily soluble in alcohol and ether, almost insoluble in water. It is very easily converted into azobenzene, even by the oxygen of the air. By warming with hydrochloric acid, it is converted into benzidine, $NH_2—C_6H_4—C_6H_4—NH_2$. It is decomposed by heat into azobenzene and aniline.

121. **Preparation of an Azo Compound.**—Azobenzene,

$$C_6H_5—N=N—C_6H_5.$$

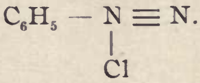
Literature.—Mitscherlich: Ann., 12, 311; Zinin: J. prakt. Chem., 36, 93, (*1845*); Claus: Ber., 8, 37; Griess: *Ibid*, 9, 132; Frankland and Louis: J. Chem. Soc., 37, 560, (1880); Spiegel: Ber., 18, 1481; Mills: J. Chem. Soc., 65, 51, (*1894*); Steromeric forms, Gortner and Gortner: J. Am. Chem. Soc., 32, 1294.

10 grams hydrazobenzene.
170 cc. alcohol.
1 cc. sodium hydroxide (3 cc. = 1 gram).

Put in a 300 cc. flask 10 grams of hydrazobenzene, 170 cc. of alcohol, and 1 cc. of a solution of caustic soda. Close the flask with a stopper bearing an upright condenser, and a glass tube leading nearly to the bottom of the flask. Heat on a water-bath and draw or force through the solution a slow current of air for three to four hours. Filter, if necessary, distil off most of the alcohol and allow the azo-benzene to crystallize after adding a little water. Yield 7 to 8 grams.

Azobenzene crystallizes in red plates, which melt at 68°. It boils without decomposition at 295°. It is soluble in 12 parts of alcohol at 16°.

122. **Preparation of a Diazonium Compound.**—Benzene diazonium chloride,



$$C_6H_5 - \underset{\displaystyle Cl}{\underset{|}{N}} \equiv N.$$

Literature.—Griess: Ann., 113, 201; 117, 1; 121, 257; 137, 39; Ber., 24, R., 1007; V. Meyer and Ambühl: *Ibid*, 8, 1073; Knoevenagel: *Ibid*, 23, 2994; Hausser and Müller: Bull. soc. chim. [3], 9, 353, (*1893*).

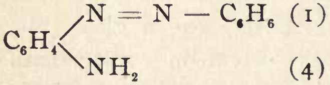
2 grams aniline hydrochloride.
8 cc. alcohol.
2 cc. (1.8 grams) amyl nitrite, or
1.3 cc. (1.23 grams) ethyl nitrite.

Dissolve 2 grams of aniline hydrochloride in 8 cc. of absolute alcohol in a test-tube. Cool with ice-water, add a drop of concentrated hydrochloric acid, and then very slowly, with cooland and stirring, 2 cc. of amyl nitrite, or 1.3 cc. of ethyl nitrite.[1] Allow to stand in ice-water for a short time, and then filter off the benzene diazonium chloride and wash it with a very little alcohol, containing a little hydrochloric acid, and with ether.

Separate into several portions and dry on filter-paper, in the air. On account of the explosive character, the portions dried should not exceed 0.1-0.2 gram each.

Small portions may be warmed with water, alcohol, or concentrated hydrochloric acid, to illustrate the decompositions of the substance, but for most purposes of synthesis, the free diazonium compounds, or salts, are not prepared. See pp. 70, 131, 201.

123. Preparation of an Amino-azo Compound through the Diazoamino Compound.—*p*-Aminoazobenzene,



$$C_6H_4\begin{cases} N = N - C_6H_6 & (1) \\ NH_2 & (4) \end{cases}.$$

Literature.—Griess: Ann., 121, 258; Staedel and Bauer: Ber., 19, 1952; Niementowski and Roszkowski: Z. physik. Chem., 22, 145.

50 cc. aniline.

60 cc. concentrated hydrochloric acid.

13 grams aniline hydrochloride.

200 cc. water.

3.5 grams sodium nitrite.

17.5 cc. water.

10 grams crystallized sodium acetate.

5 grams diazoaminobenzene.

15 grams aniline.

3 grams aniline hydrochloride.

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[1] Ethyl nitrite may be prepared as follows: Prepare a solution of 10 grams of sodium nitrite in 50 cc. of water and 5 cc. of alcohol, and a second solution of 5 cc. of concentrated sulphuric acid, 50 cc. of water and 5 cc. of alcohol. Cool each to 0°, and add the acid solution to the nitrite solution, with a pipette, which is inserted beneath the surface of the liquid, cooling thoroughly. After a few minutes, separate the ethyl nitrite, which rises to the top of the liquid, using a cold separatory funnel. Keep the nitrite in a tube, surrounded with ice. It boils at 17°. If larger quantities of the nitrite are desired, the solutions may be prepared in the proportions given, and the nitrite solution put in a flask or distilling bulb, connected with a condenser, fed with ice-water. The solutions should be at 20°-25°. On running the acid solution in slowly, the ethyl nitrite will distil over, and may be collected in a receiver, surrounded with ice. (Wallach and Otto: Ann., 253, 251.)

Prepare some aniline hydrochloride by dissolving 50 cc. of aniline in 6 cc. of concentrated hydrochloric acid, cooling thoroughly, filtering with a plate on a hardened filter, and drying on the water-bath.

Dissolve 13 grams of the aniline chloride in 200 cc. of water, bring the temperature to 25°, and add, with stirring, 3.5 grams of sodium nitrite, dissolved in 17.5 cc. of water. Keep the temperature at 27°-30° by cooling, if necessary. Add, at once, a previously prepared solution of 10 grams of crystallized sodium acetate, stir thoroughly and allow the whole to stand for 15 minutes. Filter off the diazoaminobenzene, wash and dry *in vacuo* over sulphuric acid. The yield is 9 to 10 grams. To obtain a pure, light yellow product it is best to dissolve immediately, without drying, in ligroin, on the steam-bath, pour off from the water and cool the ligroin solution till crystallization is complete.

Dissolve 5 grams of the dry diazoaminobenzene in 15 cc. of aniline, in a small flask, add 3 grams of dry, powdered aniline hydrochloride, warm in a water-bath at 40°, for an hour, and allow the mass to stand for a day, or until the solution no longer evolves nitrogen when a small portion is warmed with alcohol and hydrochloric acid. Add 40 cc. of hydrochloric acid (sp. gr. 1.10), cool, filter, and wash with dilute hydrochloric acid. Dissolve the hydrochloride of the aminoazobenzene in about 500 cc. of hot water, adding enough hydrochloric acid to prevent hydrolysis but not more. Filter, if necessary, and add 20 to 25 cc. of concentrated hydrochloric acid. On cooling, the hydrochloride will separate almost completely in crystalline form. Filter, wash with dilute acid, and dry.

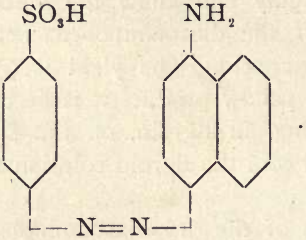
If the free aminoazobenzene is desired, it can be obtained by warming the chloride with twice its weight of alcohol, and adding concentrated ammonia till it dissolves. On further addition of water, the base separates in orange-yellow leaflets, which may be recrystallized from benzene. Yield of the chloride about 4½ grams.

p-Aminoazobenzene crystallizes in orange-yellow, rhombic prisms, which melt at 127°, and boil without decomposition at

360°. It is almost insoluble in water, easily soluble in alcohol and ether. It is reduced by tin and hydrochloric acid to aniline and paraphenylenediamine. The chloride is hydrolyzed by water It is known as aniline yellow, and in slightly acid solution colors wool and silk intensely yellow.

Diazoaminobenzene melts at 98°, and is slightly explosive.

124. Preparation of an Azo Compound by the Combination of a Diazonium Compound with an Amine.—*p*-Sulphobenzene-azo-*α*-napthylamine,



(4)-Sulphobenzene-azo-(4)-amino-(1)-naphthalene.

Literature.—Griess: Ber., 12, 427.

5 grams sulphanilic acid.
10 cc. sodium hydroxide (10 per cent.).
200 cc. water.

10 cc. hydrochloric acid (sp. gr. 1.1).

1.7 grams sodium nitrite.
8.5 cc. water.

3.5 grams *α*-naphthylamine.
6 cc. hydrochloric acid (sp. gr. 1.1).
200 cc. water.

Dissolve 5 grams of sulphanilic acid in 10 cc. of sodium hydroxide and 20 cc. of water, by warming in a flask. Cool, dilute to about 200 cc., add 10 cc. of hydrochloric acid (1.1) and then 1.7 grams of sodium nitrite dissolved in 8.5 cc. of water. Dissolve 3.5 grams of *α*-naphthylamine in 6 cc. of hydrochloric acid and 200 cc. of hot water. Cool, and add the solution of paradiazonium benzene sulphonic acid. Mix thoroughly by pouring from one beaker to another and back several times. Allow to stand for several hours, then heat on the water-bath, or over the free flame, till the precipitate becomes crystalline, and much less voluminous. Filter hot, and wash.

α-Naphthylamine-azobenzene-*p*-sulphonic acid crystallizes in microscopic needles of a dark violet color. It is almost insoluble, even in boiling water, and is also very difficultly soluble in alcohol. The dilute solutions are of a bright red or pink color, and, since the compound is formed quantitatively when nitrous acid acts on an excess of an acid solution containing sulphanilic acid and α-naphthylamine, it is often used for the determination of nitrites in potable water.

Since the substance is a sulphonic acid, it dissolves to clear orange-red solutions in very dilute solutions of caustic soda, or ammonia, but the addition of more sodium hydroxide to such solutions, even if quite dilute, will cause the precipitation of the red, crystalline, sodium salt, $C_{16}H_{12}N_3SO_3Na$.

125. Preparation of an Azo Compound by Coupling a Diazonium Compound with an Amine.—Helianthine (Methyl orange, Sodium salt of 4,4-Dimethylaminoazobenzene sulphonic acid).

$$(CH_3)_2NC_6H_4—N=N—C_6H_4—SO_3Na.$$

Literature.—Griess: Ber., 10, 258; Theory of indicators, Kremann: Z. anorg. Chem., 33, 87; Bredig: Z. anorg. Chem., 34, 202; Stieglitz: J. Am. Chem. Soc., 25, 1112; Veley: Z. phys. Ch., 57, 148; A. A. Noyes: J. Am. Chem. Soc., 32, 815; Preparation by the sulphonation of dimethylaminoazobenzene, Nölting: Ber., 20, 2996.

Solution of diazobenzene sulphonic acid.
15 grams ice.
10 cc. sodium hydroxide (10 per cent.).

3 grams dimethyl aniline.
1½ grams glacial acetic acid.

3 grams sodium hydroxide.
15 cc. water.

Prepare a solution of *p*-diazobenzene sulphonic acid as described in the preceding preparation. Add 15 grams of ice and 10 cc. of sodium hydroxide, (10 per cent.), then, at once, a mixture of 3 grams of dimethyl aniline and 1½ grams of glacial acetic acid. After 5-10 minutes add 10 cc. of a solution of sodium hydroxide (3 cc. = 1 gram). Filter on a hardened filter, suck dry and recrystallize the sodium salt (methyl orange) from water.

If anthranilic acid is used instead of sulphanilic acid for this preparation, methyl red, $(CH_3)_2N.C_6H_4—N{=}N—C_6H_4CO_2H$ will be obtained. It is a valuable indicator for weak bases. (Ber., 40, 2698.)

126. Preparation of a Hydrazine.—Phenyl hydrazine,

$C_6H_5NHNH_2$.

Literature.—E. Fischer: Ann., 190, 67; Ber., 17, 572; V. Meyer. u. Lecco: *Ibid*, 16, 2976; Reychler: *Ibid*, 20, 2463; Overton: *Ibid*, 26, 19; Altschul: *Ibid*, 25, 1849.

18.6 grams aniline.
160 cc. hydrochloric acid (sp. gr. 1.19).

14 grams sodium nitrite.
70 cc. water.

50 grams tin or 120 grams stannous chloride.
150 cc. hydrochloric acid (sp. gr. 1.19).

40 cc. sodium hydroxide (3 cc. = 1 gram).

Prepare a solution of stannous chloride by dissolving 50 grams of feathered tin in 150 cc. of concentrated hydrochloric acid or by dissolving 120 grams of crystallized stannous chloride in 100 cc. of concentrated hydrochloric acid. Add 18.6 grams of aniline (1 mol.) to 100 cc. of concentrated hydrochloric acid, stirring vigorously. Set the beaker in ice-water, or a freezing mixture, and when the temperature has fallen nearly to 0°, add 150 grams of ice, and then, from a drop funnel, drawn to a narrow tube at the end, or having a narrow tube attached, and dipping nearly to the bottom of the solution, add slowly and with constant stirring, a cold solution of 14 grams (1 mol.) of sodium nitrite in 70 cc. of water. The temperature should not rise above 5°. When all has been added, the solution, after standing two minutes, should react for nitrous acid, when a drop is diluted and tested with starch potassium iodide paper. If it does not, a little more sodium nitrite must be added, using the least possible excess. As soon as possible, add slowly, with stirring, the solution of stannous chloride, which must, meanwhile, have been cooled to 0°, or below. Add, if necessary, more ice, to keep the temperature below 0° during the addition of the stannous chloride. Stir very thoroughly, and allow to stand for an hour. Filter off the hydrochloride of the phenyl hydrazine, which separates, suck and press it as free as possible from the mother-liquors, and wash once with a small amount of dilute hydrochloric acid. Evaporate the filtrate to about 150 cc., best in a large beaker heated over a free flame on wire gauze Cool, and separate the hydrochloride of the phenyl hydrazine, which crystallizes, as before. Dissolve the hydrochloride in a small amount of warm water, add an excess of a strong solution of sodium hydroxide, cool, collect the phenyl hydrazine with a little ether, separate, distil off the ether, dry by allowing to stand *in vacuo* over sulphuric acid, or dry with fused caustic potash, pour off and distil, best under diminished pressure. Some ammonia is formed during the distillation, which may be removed by allowing the product to stand over sulphuric acid. The phenyl hydrazine may be further purified by a second distillation, or by allowing it to solidify at a low temperature, and pouring off the liquid portion. Yield, about 18 grams.

Phenyl hydrazine boils at 242°, and solidifies at a low temperature, melting at 19°. Its specific gravity is 1.097, at 23°. It is a violent poison. On adding a solution of phenyl hydrazine acetate to a hot solution of copper sulphate, it is oxidized with the formation of benzene. With aldehydes, ketones, and sugars, phenyl hydrazine gives characteristic condensation products. See pp. 89, 191.

127. Preparation of a Derivative of Hydroxylamine by the Electrolytic Reduction of a Nitro Compound.—β-Phenylhydroxylamine, C_6H_5NHOH.

Literature.—Brand: Ber., 38, 3077; Bamberger: Ber., 27, 1347, 1548; Wohl: Ber., 28, R, 1079; Apparatus for electrolytic reduction, Brand: Elektro-Chemische Reduktion organische Nitroverbindungen und verwandter Verbindungen; Ahren's Sammlungen, 13, 51; Elbs: Uebungsbsp. elektrolyt. Darst. chem. Präparate, Bredt: Ann., 366, 13.

Dilute sulphuric acid (1:20 by volume).

50 grams nitrobenzene.
20 grams sodium acetate.
15 cc. glacial acetic acid.
350 cc. water.

Wind a small lead pipe around a porous cell having a capacity of 750 cc. and place this within a battery jar or porcelain beaker just wide enough to contain it. The space between the jar and porous cell is to be filled with dilute sulphuric acid (1:20 by volume). The lead pipe serves as anode and the whole apparatus is kept cool by passing cold water through it. For cathode a piece of nickel gauze with a surface on one side of 3 or 4 square decimeters is used. This is bent in such a manner that an efficient mechanical stirrer (27, p. 76) can play within it in the porous cup. Place in the porous cell 50 grams of nitrobenzene, 20 grams of sodium acetate, 15 cc. of glacial acetic acid and 350 cc. of water. This mixture must be kept thoroughly stirred during the passage of the current. A current of 6 to 10 amperes, or of 2 to 3 amperes per square decimeter of cathode surface should be used. The voltage required will depend on the resistance but 10 to 12 volts should be enough. The current is best supplied by a storage battery, if available. No hydrogen will appear at the cathode till the theoretical quantity of electricity has been used and the current should be broken soon after that point has been reached. One ampere of electricity will furnish 0.000606 gram of hydrogen per minute. Filter the cathode liquid, wash out the porous cup with a little warm water and add to the united filtrate clean, finely powdered salt nearly to saturation. The β-phenylhydroxylamine crystallizes in long, silky, colorless needles which melt at 81°. It may be recrystallized from ligroin. Yield 25 to 30 grams. Care must be taken not to bring solutions of phenylhydroxylamine in contact with the skin as it causes on some people painful irritation and swelling.

Chapter XV

SULPHUR COMPOUNDS

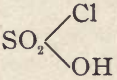
In the aliphatic series sulphonic acids are obtained by the oxidation of mercaptans (sulphur alcohols), with nitric acid, or with potassium permanganate.

$$RSH + 3O = R—SO_2.OH.$$

They are also formed by heating the sodium salt of an acid ester of sulphuric acid with sodium sulphite in concentrated solution at a temperature of 110°-120°.(Mayer: Ber., 23, 909).

$$R—O—SO_2—O—Na + Na_2SO_3 = R—SO_2ONa + Na_2SO_4.$$

Fatty acids react with sulphur trioxide and their anhydrides with sulphuric acid, or with the chloride of sulphuric acid



$SO_2\langle{}^{Cl}_{OH}$, to form sulphonic acids, which contain both sulphonic and carboxyl groups, and are bibasic. The sulphonic group usually combines with the α-carbon atom.

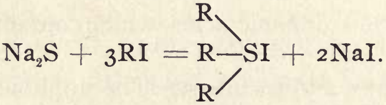
In the aromatic series sulphonic acids are almost exclusively prepared by the action of sulphuric acid, sulphur trioxide, the fuming acid or the chloride of the acid on hydrocarbons and their derivatives. The sulphonic group usually enters into the para or ortho position with regard to NH_2, OH, CH_3, OR, Cl, Br, and I, but in the meta position with regard to CO_2H, SO_3H, COH, $COCH_3$, CN, CCl_3, or NO_2. As with nitration, homologues of benzene are more easily sulphonated than benzene itself. The strength of the acid to be used, and the temperature vary with different cases, and must be established by trial with small amounts, or by a consideration of the conduct of analogous compounds.

$$RH + H_2SO_4 = R—SO_2OH + H_2O$$
$$RH + SO_3HCl = RSO_2Cl + H_2O.$$

The sulphonic acids are, in most cases, easily soluble in water, and as a large excess of sulphuric acid must be used for their preparation, it is usually necessary to separate the acids after dilution with water. Two methods are commonly used. The older method and the one almost universally applicable, consists in neutralizing the diluted solution with calcium carbonate, or barium carbonate, and filtering from the insoluble sulphates, the calcium and barium salts of the sulphonic acids being usually soluble in water. From these salts the sodium or potassium salts can then be prepared, by use of sodium or potassium carbonate. The second method consists in saturating the diluted solution with salt, which will, in many cases, cause the precipitation of the sodium salt, even in cases where the latter is comparatively easily soluble in pure water (see p. 159 and 28, p. 79).

Sulphonium compounds are prepared by treating alkyl sulphides with alkyl iodides, or by treating metallic sulphides with an excess of alkyl iodide.

$$R_2S + RI = R_3SI.$$



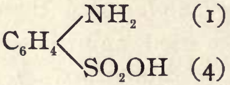
$$Na_2S + 3RI = R_3SI + 2NaI.$$

The sulphonium hydroxide can be prepared from the iodides, or other halogen salts, by treatment with silver oxide and water.

These hydroxides are strong bases, resembling the quaternary ammonium hydroxides, and the iodoso and iodonium compounds.

The preparation of benzene sulphonic acid and the sulphone-chloride and amide has been given in a previous chapter, (p. 159).

128. Preparation of a Sulphonic Acid of an Amine.—Sulphanilic acid,



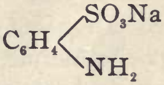
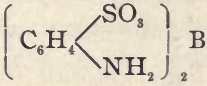
$C_6H_4\begin{cases}NH_2 & (1)\\ SO_2OH & (4)\end{cases}$. (Paraamino-sulphobenzene.)

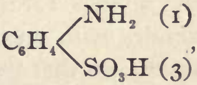
Literature.—Gerhardt: Ann., 60, 310; Buckton, Hofmann: *Ibid,* 100, 163; Limpricht: *Ibid,* 177, 80; Laar: Ber., 14, 1933; Schmidt: Ann., 120, 132; Winther: Ber., 13, 1941.

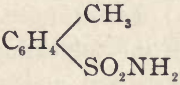
30 grams aniline.

90 grams (50 cc.) concentrated sulphuric acid.

Put 90 grams of concentrated sulphuric acid in a small flask, add in small portions, with shaking, 30 grams (30 cc.) of aniline, and heat in an oil-bath at 180°-190° for four to five hours, or until a drop of the solution, after diluting, and adding caustic soda, shows no separation of aniline. Allow to cool, pour into 250 cc. of cold water, cool, filter, and wash. Recrystallize from hot water, adding a little bone-black. Yield 30-35 grams.

Sulphanilic acid crystallizes with two molecules of water, in rhombic plates, which effloresce readily. It dissolves in 166 parts of water at 10°. It carbonizes on heating to 280°-300°. It forms no salts with acids. The sodium salt,  $C_6H_4\left\langle\begin{matrix}SO_3Na\\NH_2\end{matrix}\right.$ + $2H_2O$, and the barium salt,  $\left[C_6H_4\left\langle\begin{matrix}SO_3\\NH_2\end{matrix}\right.\right]_2 Ba + 3\frac{1}{2}H_2O$, crystallize well.

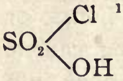
Sulphanilic acid is used in water analysis for the estimation of nitrites (see **124**, p. 252). The sulphonic derivatives of amines are of great technical importance, since the sulphonic group furnishes the "auxochrome" group necessary for dyestuffs (see p. 245). Sulphanilic acid, metanilic acid,  $C_6H_4\left\langle\begin{matrix}NH_2\ (1)\\SO_3H\ (3)\end{matrix}\right.$, and the sulphonic acids of α- and β-naphthylamine are especially used in the preparation of azo dyes.

129. Preparation of Sulphonechlorides and Sulphonamides by the use of the Chloride of Sulphuric Acid.—*o*- and *p*-toluene sulphonamides,  $C_6H_4\left\langle\begin{matrix}CH_3\\SO_2NH_2\end{matrix}\right.$.

Literature.—Remsen and Fahlberg: Am. Chem. J., **1**, 427; Claesson and Wallin: Ber., **12**, 1848; Noyes: Am. Chem. J., **8**, 176; Fahlberg, Patents: Ber., **19**, R. 374, 471; Müller: *Ibid*, **12**, 1348; Terry: Ann., **169**, 27.

100 grams sulphuric acid monochloride.
40 grams toluene.

Put in a flask 100 grams of the chloride of sulphuric acid,


$SO_2{<}^{Cl}_{OH}$[1], place it in cold water, and drop in very slowly, with thorough cooling, 40 grams of toluene. When all has been added, pour the solution carefully into cold water. The mixed sulphonechlorides will mostly solidify after a short time. Filter on a plate with the pump, and by the continuous action of the pump, and the repeated addition of small amounts of water, suck through so much as possible of the liquid chloride. The solid chloride remaining is nearly pure paratoluenesulphonechloride, and after thorough drying on porous porcelain it may be kept in tightly-stoppered bottles, or it may be converted into the amide by treatment with strong aqua ammonia.

Separate the liquid chloride from the solution, put it in a test-tube or small flask, and cool it to —20° for two hours, with a freezing mixture. Filter as quickly as possible, the liquid chloride from the solid which separates, with the aid of the pump. Treat the liquid chloride obtained in this way with a slight excess of strong aqua ammonia, filter, and crystallize the amides formed from hot water. In crystallizing, treat the amides with enough water, added in small portions to avoid an excess, so that they barely dissolve on boiling; then cool to about 70°, and keep at that temperature for some time. Most of the orthoamide will separate, and on filtering it off, and recrystallizing once, it will be pure. The amides which separate on cooling the filtrate cannot usually be separated further by crystallization, but by boiling, for half an hour, with potassium pyrochromate (3 parts), sulphuric acid (4½ parts), and water (8 parts), the parasulphonamide may be oxidized to the sulphamide of benzoic acid, while the orthoamide is partly destroyed, and partly remains unchanged. By cooling, filtering, washing, and boiling the residue with barium carbonate and water, the acid is converted into a salt, and on filtering hot, and cooling, the orthoamide will separate. Yield of orthoamide about 6 grams.

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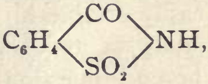
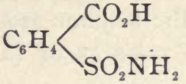
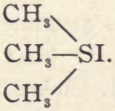
[1] The chloride of sulphuric acid can be prepared by putting strongly fuming or crystallized pyrosulphuric acid in a distilling bulb, fitting a tube passing into the acid to the neck of the bulb with a stopper, made by wrapping it with thick, soft asbestos paper, and passing in dry hydrochloric acid gas while the contents of the bulb is warmed. The chloride will distil over. The arrangement of condenser and receiver should be similar to that for acetyl chloride (see 58, p. 148).

Toluene orthosulphonechloride is an oil, the parachloride melts at 89°, and boils at 145°-146°, under a pressure of 15 mm. Toluene orthosulphonamide crystallizes in octahedral crystals, which melt at 155°, and dissolve in 958 parts of water at 9°. Tolueneparasulphonamide crystallizes in leaflets, which melt at 137°, and dissolve in 515 parts of water at 9°.

The orthoamide is oxidized by potassium permanganate, in faintly alkaline solution, to benzoic sulphinide,  $C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH$, ("saccharin") which is 500 times as sweet as cane-sugar. In strongly alkaline solutions it is oxidized by potassium permanganate, or potassium ferricyanide, to the orthosulphamide of benzoic acid,  $C_6H_4\left\langle\begin{matrix}CO_2H\\SO_2NH_2\end{matrix}\right.$.

130. Preparation of a Sulphonium Compound.—Trimethylsulphonium iodide,  $\begin{matrix}CH_3\diagdown\\CH_3-SI.\\CH_3\diagup\end{matrix}$

Literature.—Oefele: Ann., 132, 82; Cahours: *Ibid,* 135, 355; Klinger: Ber., 10, 1880; 15, 881; Masson and Kirkland: J. Chem. Soc., *1889,* 135; Dehn: Ann. Supl., 4, 106; Schöller: Ber., 7, 1274; Klinger and Masson: Ann., 243, 193; 252, 257; Brown and Blaikie: J. prakt. Chem. [2], 23, 395.

3 grams potassium hydroxide.
20 cc. methyl alcohol.
0.8 gram hydrogen sulphide.

13 grams methyl iodide.

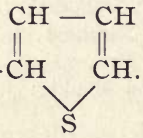
Put in a 200 cc. flask 3 grams of potassium hydroxide, and dissolve it in 20 cc. methyl alcohol. Weigh on scales sensitive to one-tenth of a gram, and pass into the solution 0.8 gram of hydrogen sulphide. Filter into a 100 cc. flask, connect with an effective upright condenser, and pour in through the latter

13 grams (5½ cc.) of methyl iodide. Warm gently till the reaction begins, and then continue to boil gently for half an hour. Pour off the warm solution from the potassium iodide which separates. On cooling, the trimethylsulphonium iodide will crystallize. Pour the mother-liquors back into the flask, heat to boiling, allow to cool slightly, and pour off as before. Recrystallize the trimethylsulphonium iodide once or twice from methyl alcohol.

Trimethylsulphonium iodide crystallizes in prisms, which are easily soluble in water, more difficultly soluble in alcohol. The study of the sulphoniuum compounds has established, almost beyond question, the quadrivalence of the sulphur in them. Their study has also rendered it probable that the relation of the groups to the sulphur is such that no change is produced in the molecule when two of the groups exchange places, or, as usually stated, that the four valences of the sulphur atom are of equal value in the same sense that the valences of the carbon atom are alike.

When four different groups are combined with a sulphur atom, however, the molecule becomes asymmetric and the resulting compound may, in some cases, at least be separated into optical isomers, Pope and Peachy: J. Chem. Soc., 77, 1072.

131. Thiophene.—



Literature.—V. Meyer: Ber., 16, 1465, 1471; *Ibid,* 17, 2641; 18, 217; V. Meyer and Sandmeyer: *Ibid,* 16, 2176; Volhard and Erdmann: *Ibid,* 18, 454; Schulze: *Ibid,* 18, 497; Paal and Tafel: *Ibid,* 18, 456.

100 grams phosphorus trisulphide.[1]
100 grams dry sodium succinate.

Powder finely and mix together 100 grams of phosphorus trisulphide, and 100 grams of sodium succinate, dried thoroughly at 140°. Put the mixture in a flask or non-tubulated retort, which should be filled only half full. Connect with a condenser, which has a distilling bulb tightly fastened to its lower end and surrounded with a freezing mixture. From the side tube of the distilling bulb connect tubes leading out of doors or to the chimney. Heat till the reaction begins, and then allow it to proceed of itself till completed.

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[1] The phosphorus trisulphide can be prepared by melting together, in a Hessian crucible, the theoretical amounts of dry, red phosphorus and sulphur. The sodium succinate can be obtained by neutralizing succinic acid with a strong solution of sodium carbonate or caustic soda, and evaporating the solution to dryness.

Distil the thiophene from the water-bath, wash it with a solution of caustic soda, dry it with sodium, and distil.

Thiophene is a mobile, colorless liquid, which boils at 84°, and has a specific gravity of 1.062 at 23°. On warming a minute portion of it with isatine and concentrated sulphuric acid, a bluish green color is produced. This reaction is used to detect thiophene in benzene.

Chapter XVI

QUALITATIVE EXAMINATION OF CARBON COMPOUNDS

Because of the very great number of carbon compounds, it is impossible to give any scheme for qualitative examination which is at all general in its application. In dealing with an unknown substance or mixture, the first attempt should be to determine what elements other than carbon are present, and whether the substance is a single one or a mixture. For the latter purpose boiling-points and melting-points are most generally applicable, substances with a constant boiling-point, and with a sharp melting-point, being usually pure, though there are some exceptions. For the determination of what elements, other than carbon and hydrogen, are present, the method most generally applicable consists in heating about 0.1 gram of the substance with 1 cc. of fuming nitric acid(sp. gr. 1.48 at least) at 200°-300° for two hours, in a sealed tube having a capacity of 20 to 30 cc. (p. 20). The tube must be heavy-walled and carefully sealed, with a capillary at one end. When cold, this end is softened carefully in the flame till the gases blow out. The nitric acid will contain sulphur, phosphorus, and arsenic in the form of their respective acids, chlorine, and bromine partly in the form of hydrochloric and hydrobromic acids, and partly free, iodine in the form of iodic (not hydriodic) acid, and metallic elements in the form of nitrates. All of these may be detected, when present, by means of the usual qualitative tests of inorganic chemistry.

Another method, which is much quicker and almost as general in its application for non-metallic elements, consists in heating with metallic sodium. Put in a short, dry tube of hard glass, about 1/20 gram of clean sodium. Heat quickly over a small flame till part of the sodium is converted into vapor, and drop straight down into the tube one or two drops of the substance, if a liquid, or a corresponding amount if a solid. Allow to cool, add a little alcohol to dissolve unchanged sodium, then a few cc. of water, and filter. The solution may be tested for various elements as follows:

Sulphur, with a silver coin, with a solution of sodium nitroprusside, or with a solution of lead acetate in sodium hydroxide.

Cyanides (in absence of sulphur), by warming with sodium hydroxide and a small amount of a mixture of ferrous and ferric salts, and subsequent acidification with hydrochloric acid, when prussian blue wil be formed, if nitrogen was present in the original substance. In some cases metallic potassium reacts more readily than sodium for the detection of nitrogen.

Chlorine, with nitric acid and silver nitrate; if sulphur or nitrogen are present, it is necessary to boil with nitric acid before adding the silver nitrate.

Bromine and iodine, with hydrochloric acid, carbon bisulphide, and chlorine water, or potassium nitrite for iodine.

Sulphur and nitrogen together will form a thiocyanate, which gives a red color with ferric chloride after acidifying with hydrochloric acid.

The following special tests are also frequently useful:

Nitrogen.—Many nitrogenous compounds, but not all (especially not nitro compounds), give ammonia when heated in a small tube with soda-lime. The ammonia is best detected by means of moist, reddened litmus paper in the mouth of the tube.

Halogens.—Make a small loop in the end of a copper wire, and oxidize it by holding it in the outer edge of a Bunsen flame. Cool, dip in a little of the substance to be tested, and hold in the flame. The latter will be tinged green if a halogen is present. Halogens may also be detected by igniting the substance with pure quicklime in a tube of hard glass, dissolving the residue in nitric acid and testing in the usual manner. In many cases, also, by heating with sodium carbonate till carbonization takes place, adding some potassium nitrate, and heating again till white, dissolving in water, and testing with nitric acid and silver nitrate. Another method is to put 0.05 gram of the substance in a test-tube, add one gram of sodium peroxide and heat till the mixture is white. Cool, add acetic acid and a little potassium persulphate and boil. Iodine, if present, will be expelled and may be detected by the color of the vapors or by means of carbon disulphide before boiling. After expelling the iodine, bromine may be liberated by adding dilute sulphuric acid and detected by means of starch potassium iodide paper held in the vapors. After expelling the bromine by boiling, chlorine may be found in the solution which remains by adding silver nitrate. (Jannasch: Ber., 39, 196, 3655.)

Having determined what elements are present, and, if possible, whether the substance under examination is a single compound or a mixture, and, in case of mixtures, having, if possible, separated the constituents, the remainder of the examination will consist mainly in the endeavor to obtain some idea of the nature of the substance, and then to identify it as agreeing entirely in its properties with some compound described in the text-books or handbooks on organic chemistry. The following general principles will be of service:

Acids are, in most cases, sufficiently soluble in water to redden blue litmus, and in almost all cases they are soluble in ammonium or sodium hydroxide, and decompose sodium carbonate with evolution of carbon dioxide. Polybasic acids are usually more soluble in water than monobasic ones, and the solubility usually decreases with an increase of molecular weight. The lead and silver salts of many acids are difficultly soluble, and may be obtained by precipitation from solutions of sodium or ammonium salts. The calcium salts of bibasic acids are often difficultly soluble. The substances most liable to be mistaken for acids are phenols, some esters of ketonic acids, and acid amides, these compounds being, in many cases, soluble in alkalies, and precipitated again by acids.

Esters are identified by saponification by boiling with alkalies or acids, and subsequent determination of the alcohol and acid from which they are derived.

Amides, imides and nitriles are also identified by boiling with alkalies or acids, which decompose them with formation of ammonia. The derivatives of different acids differ very greatly, of course, in the ease with which they are saponified.

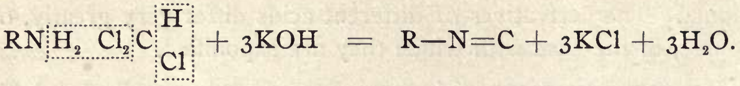
Halogen derivatives of hydrocarbons are universally insoluble in water. Many of them are decomposed by alcoholic potash with formation of unsaturated hydrocarbons, but the halogen atoms in the nucleus of benzene derivatives usually react with difficulty, if at all.

Nitro compounds may be reduced to amines by tin and hydrochloric acid. Most nitro compounds give yellow solutions on warming with alcoholic potash. The nitro compounds themselves are insoluble, or very difficultly soluble in water. They evolve no ammonia, or very little on warming with soda-lime.

Amines are best characterized by the formation of salts with acids. The salts with chloroplatinic (H_2PtCl_6) and chlorauric ($HAuCl_4$) acids are frequently, though by no means always, difficultly soluble and characteristic.

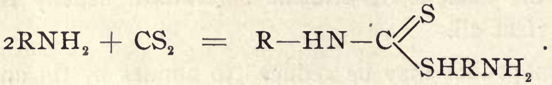
Aliphatic amines and aromatic amines with the amino group in the side chain, react strongly alkaline with litmus. Aromatic amines, with the amino group in the nucleus, do not turn red litmus blue. They form well defined salts, however. To distinguish primary, secondary and tertiary amines, see p. 160. Another method of distinguishing them consists in treatment with nitrous acid. Primary amines form alcohols, or unsaturated hydrocarbons, or diazonium compounds which decompose with water to form phenols. Secondary amines form nitroso amines, which, on solution in phenol, treatment with a little concentrated sulphuric acid, subsequent dilution, and neutralization with caustic potash, give a blue color. (Liebermann's reaction: Ber., 7, 248; Baeyer: *Ibid,* 7, 966.) The reaction appears to be due to the formation of a nitrosophenol by the action of the nitrosoamine, and a subsequent condensation under the influence of the sulphuric acid. Tertiary amines do not react with nitrous acid.

When a primary amine is warmed with a little chloroform and alcoholic potash, an isonitrile is formed, which can be recognized by its penetrating and exceedingly disagreeable odor. (Hofmann.)



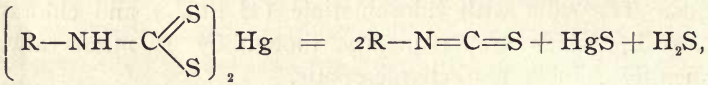
$$RN\,H_2\ Cl_2C\begin{matrix}H\\Cl\end{matrix} + 3KOH = R{-}N{=}C + 3KCl + 3H_2O.$$

When a primary amine is treated with a little carbon disulphide, dissolved in alcohol or ether, a salt of an alkyl dithiocarbamic acid is formed.



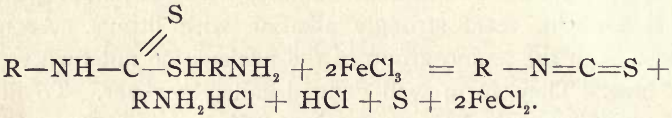
$$2RNH_2 + CS_2 = R{-}HN{-}C\begin{matrix}/\!\!/S\\ \diagdown SHRNH_2\end{matrix}.$$

If, after evaporating part of the alcohol, the solution is warmed with not too much mercuric chloride, or better with ferric chloride, a mercuric salt of the dithiocarbamic acid is at first formed, and this is then decomposed with the formation of an isothiocyanate (mustard oil) with a characteristic odor.



$$\left[R{-}NH{-}C\begin{matrix}/\!\!/S\\ \diagdown S\end{matrix}\right]_2 Hg = 2R{-}N{=}C{=}S + HgS + H_2S,$$

or



$$R{-}NH{-}\overset{\overset{S}{/\!\!/}}{C}{-}SHRNH_2 + 2FeCl_3 = R{-}N{=}C{=}S + RNH_2HCl + HCl + S + 2FeCl_2.$$

Hydrazo, azo, diazonium compounds, etc., may usually be recognized by their characteristic properties, as given in the chapter on these substances and in larger works.

Alcohols, phenols, and all compounds containing hydroxyl react with sodium with the evolution of hydrogen. Some substances not usually supposed to contain hydroxyl, as aldehydes and some ketones, react in the same manner, however. The formation of an acetyl or benzoyl derivative (most easily by the Schotten-Baumann reaction when it can be applied, pp. 154 and 155), is especially characteristic of alcohols and phenols. It must be remembered, however, that primarv and secondary amines show a similar reaction.

Methyl or ethyl alcohol may be detected in dilute aqueous solutions, as follows: Distil 10 to 20 cc. from 100-200 cc. of the solution. Put the distillate in a smaller bulb, and distil 4 to 6 cc. To this distillate, in a test-tube, add dry potassium carbonate till the alcohol separates on top. Transfer the upper layer to a small distilling bulb by means of a pipette, and determine its boiling-point, boiling it with a very small flame, and using a thermometer with as small a bulb as possible. Ethyl alcohol may be identified in this manner in 100 cc. of a one per cent. solution.

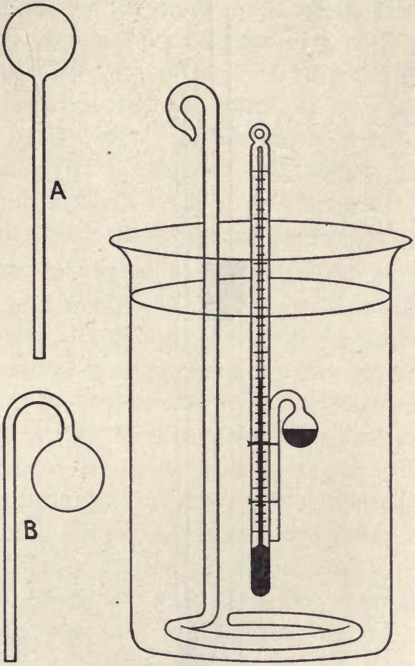


Fig. 40.

The boiling-point of a still smaller amount of a substance may be determined by the method of Siwoloboff: Ber., **19**, 795, as modified by Mulliken, "A Method for the Identification of Pure Organic Compounds," p. 222, or by the method of Smith and Menzies: J. Am. Chem. Soc., **32**, 897. The last method consists in introducing a small amount of the substance into the small bulb shown in Fig. 40, attaching the bulb to a thermometer immersing in a bath of water, sulphuric acid or other suitable material as for a melting-point determination and heating till a rapid stream of bubbles escapes from the mouth of the capillary, or, in case the vapor dissolves in the liquid in the bath, till no more bubbles of air escape from the end of the capillary tube. On

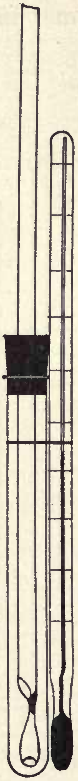


Fig. 41.

allowing the bulb to cool somewhat the temperature of the bath when the stream of bubbles ceases or when the liquid commences to rise in the capillary, is the boiling-point. Mulliken's apparatus shown in Fig. 41 is similar in principle and has the advantage that the vapor of the compound does not come in contact with the liquid of the bath.

Phenols, and hydroxy acids in which the hydroxyl is ortho to the carboxyl, give characteristic color reactions with ferric chloride in aqueous, and sometimes in alcoholic solutions. Phenols dissolve in alkalies with the formation of unstable salts. The alkaline solutions of phenols are usually very sensitive to oxidation, and to the action of the air.

Aldehydes and ketones are usually most easily recognized by the action of phenyl hydrazine in dilute acetic acid solution (see **24**, p. 73), or the formation of compounds with acid sodium or potassium sulphite (see **33**, p. 92). Hydroxylamine, and semicarbazine may also be used for purposes of identification (see **34**, and **35**, pp. 93 and 95). Aldehydes redden instantly a very dilute cold solution of a fuchsine salt, which has been decolorized by sulphurous acid (Caro). Aldehydes reduce a cold, ammoniacal solution of silver nitrate (see p. 91). (Tollens.)

Sulphonic acids are usually easily soluble, and the salts are mostly soluble, and many of them crystallize well. The most important reactions of sulphonic acids for purposes of identification are the formation of sulphonamides (see **70**, p. 159), the formation of phenols by fusion with caustic potash (see **28**, p. 78), the formation of nitriles by distillation of a sodium or potassium salt with potassium cyanide, of acids by fusion with sodium formate, and the regeneration of the original hydrocarbon by heating in a sealed tube with concentrated hydrochloric acid, or distillation with sulphuric or phosphoric acid in a current of superheated steam. (Freund: Ann., **120**, 80; Armstrong and Miller: J. Chem. Soc., **45**, 148; Kelbe: Ber., **19**, 92).

Hydrocarbons are universally insoluble in water, and dilute acids. The hydrocarbons of the marsh gas series are nearly or quite insoluble in concentrated sulphuric acid (see, however, Orndorff and Young: Am. Chem. J., **15**, 261, as to the slow absorption of propane by fuming sulphuric acid). Some of them are converted into nitro compounds by *dilute* nitric acid (p. 209). Unsaturated hydrocarbons decolorize bromine instantly, are absorbed by concentrated sulphuric acid with the formation of acid alkyl esters of sulphuric acid, and reduce cold, neutral solutions of potassium permanganate instantly, with separation of manganese dioxide. Aromatic hydrocarbons dissolve in concentrated sulphuric acid with the formation of sulphonic acids, which remain in solution on dilution. They are converted into nitro compounds, which remain undissolved on dilution, by concentrated or fuming nitric acid, or mixtures of nitric and concentrated sulphuric acids. Dinitro and trinitro compounds, which are usually solids, are, as a rule, most suitable for purposes of identification.

Alkaloids give precipitates with tannic acid, phosphomolybdic acid, potassium mercuric iodide, and with iodine in an aqueous solution of potassium iodide. Like amines they usually give characteristic crystalline salts with chloroplatinic, chlorauric and picric acids. Many alkaloids may be extracted from alkaline solutions by ether, benzene, amyl alcohol, chloroform, or acetic ester. Most of them give characteristic color reactions of various kinds. For details, reference must be had to some work on toxicology.

Reagents

In very many operations in organic chemistry, success depends on the use of reagents in definite quantities, and in almost all cases it is an advantage to know quite accurately how much of each substance is present. Students should acquire the habit, therefore, of using solutions of known strength, and of weighing or measuring the substances and solutions used. This is greatly facilitated by knowing the strength, approximately, of the common laboratory reagents, and by having always at hand certain strong solutions of substances often used. Facility in making quick, approximate calculations of quantities reacting, is necessary, and this is often aided by using the number of grams, or deci-, or centigrams of a body corresponding to its molecular weight.

Among the solutions which are especially useful in organic work, and which are of strengths different from the ordinary laboratory reagents, may be mentioned the following:

Hydrochloric Acid.—Sp. gr. 1.11. One cc. contains 0.25 gram

HCl, or 4 cc. = 1 gram HCl. One gram contains 0.224 gram HCl. This acid is aproximated closely by diluting concentrated pure hydrochloric acid with an equal volume of water.

Sulphuric Acid.—Sp. gr. 1.55. One cc, contains 1 gram H_2SO_4, or 1 gram contains 0.645 H_2SO_4. This acid is closely approximated by diluting pure concentrated sulphuric acid with an equal volume of water.

Sodium Hydroxide.—Sp. gr. 1.29. One cc. contains 0.335 gram NaOH, or 3 cc. = 1 gram. One gram contains 0.26 gram NaOH. The solution is approximated closely by dissolving 335 grams of pure sodum hydroxide in 700 cc. of water, and diluting the solution to one liter, when cold. The solution does not attack glass as readily as weaker solutions.

Sodium Nitrite.—5 cc. = 1 gram. Approximated by dissolving 205 grams of crystallized sodium nitrite in 800 cc. of water, and making the volume to one liter. The exact strength can be determined by diluting a small portion very largely, acidifying with dilute sulphuric acid, and titrating to permanent red with standard potassium permanganate. The end reaction is slow.

Many other solutions will suggest themselves to any one working in particular lines, but further details are scarcely necessary.

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Page numbers in heavy face type indicate either chapter headings or that directions are given for the preparation of the compound mentioned. The prefixes para, ortho, etc., are not regarded in the arrangement; thus, *p*-nitrobenzoic acid is given under the letter N.

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